THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

AUGUST 1933.

XV. *The Flexural Centre and the Centre of Twist of an Elastic Cylinder.*

By W. J. DUNCAN, *D.Sc., A.M.I.Mech.E.*, D. L. ELLIS, *B.Sc., A.R.T.C., and* C. SCRUTON, *B.Sc., of the Aerodynamics Department, The National Physical Laboratory* *.

§ 1. *Introduction and Summary* †.

THE paper is divided into two parts, the first dealing with theory and the second with experiments. Part I. begins with a definition of the flexural centre of a cantilever beam. The position of this point cannot, strictly speaking, be found theoretically when the conditions of support are arbitrary, but when the beam is long and has rigid or quasi-rigid support at the base a very close approximation may be obtained on the assumption that the shearing stresses are distributed in accordance with the St. Venant theory of flexure. Formulæ giving the position of the flexural centre of a cylinder whose section has an axis of symmetry, deduced on this basis, are quoted from an earlier paper ‡.

* Communicated by E. F. Relf, A.R.C.Sc.

† The authors are indebted to the Aeronautical Research Committee for permission to communicate the paper.

‡ R. & M. 1444. "The Torsion and Flexure of Cylinders and Tubes," by W. J. Duncan (February 1932).

Next, the centre of twist is defined, and a method is stated for its determination when the boundary conditions are strictly compatible with the St. Venant theory of torsion. In most practical instances the boundary conditions are not strictly compatible with this theory, and the mathematical determination of the centre of twist becomes in general a problem of great difficulty, although considerations of symmetry sometimes suffice for a solution. However, it is shown that when the cylinder is long and has rigid or quasi-rigid support at the root the reciprocal theorem leads to the conclusion that the centre of twist must be at least nearly coincident with the flexural centre.

Part II. gives an account of experimental methods for finding the flexural centre and centre of twist, and certain sources of error are discussed. The first series of tests described were made on a long mild steel cylinder of thin symmetrical aerofoil section. Both the flexural centre and the centre of twist of this cylinder were found to lie at the theoretical position of the flexural centre, within a small margin of error. The second set of measurements were made on a mild steel prism whose section had the form of a slender isosceles triangle. Here both the centres lay near the base and were thus widely separated from the centroid of the section. The centres were not quite coincident, as the centre of twist was consistently found to be nearer the base by about 0·03 of the chord. Although the theory given in R. & M. 1444 does not strictly apply to a triangular section, yet the predicted position of the flexural centre is in fairly close agreement with experiment.

So far as is known the St. Venant torsion problem has not been solved for an isosceles triangular prism when the vertical angle is general, but an approximate solution is obtained in the Appendix by the use of Ritz's method. The resulting formula for the torsional stiffness is closely verified by the experiments. For the purpose of this comparison it was necessory to obtain an independent measurement of the rigidity μ, and as the steel bar was too slender to provide a standard torsional test-piece of circular section a square section was adopted. A long square specimen is comparatively easy to machine with accuracy, and with such a specimen it is easy to find the rigidity using merely the ordinary apparatus of a physical

laboratory. The technique of this test, which is described in § 13, may be of some general interest.

In conclusion, the writers wish to express their thanks to Mr. E. L. Bottomley, of the Aerodynamics Workshop Staff of the National Physical Laboratory, by whose skill and patience the great difficulties involved in the accurate machining of the long and slender cylinder of oval section were ultimately overcome.

Part I.—Theoretical Discussion.

§ 2. *The Flexural Centre.*

Consider a cylinder of elastic material provided at the base either with rigid support or with some kind of elastic connexion to a large body which can be treated as rigid, *e.g.*, the earth. At the free end let a concentrated load be applied to a point of the section in any direction at right angles to the generators. In general the load will cause an angular displacement of the section as a whole about an axis parallel to the generators, as well as the flexural displacement and localized distortion, but there is a particular point of application of the load for which the twist is always absent. This point is the flexural centre of the section for concentrated loads. For distributed tractions the flexural centre must be defined in relation to the line of action of the resultant load, and the position of the centre may depend on the distribution of the tractions. However, for long cylinders the position of the flexural centre will be very nearly independent of the distribution of the tractions.

In the foregoing definition it is supposed that the load is applied and the twist measured at the tip of the beam. However, the definition can be extended to the case where the load is applied at an arbitrary section A, and the twist measured at some arbitrary section B. In general the position of the flexural centre in the section will depend on the choice of both A and B, but for a long beam it will tend to become independent of the choice, provided that neither A nor B is close to the root.

A general solution of the problem of the flexure of a cantilever of homogeneous and isotropic material under arbitrary systems of tractions applied to the base and free end has not hitherto been found, but an important

special solution was obtained by St. Venant. This solution has the characteristic that all the shearing stresses are independent of the distance from the base, and it must therefore correctly represent the state of stress and strain in a long beam, except possibly in the immediate vicinity of the ends. Accordingly the St. Venant theory may be made the basis of a theoretical determination of the position of the flexural centre of a long cylindrical beam when the support at the root is rigid or nearly so. It has been shown * that when the section of the cylinder has an axis of symmetry and is free from sharp angles, except possibly on the axis of symmetry at the ends, the flexural centre lies on the axis at a distance $\bar{\bar{\chi}}$ from the centroid given by the formula

$$\bar{\bar{\chi}} = \frac{\int xt^3 dx - 3\iint \Omega \, dx \, dy}{\int t^3 dx} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here t is half the thickness of the section at the distance x from the centroid and Ω is a shearing stress function which vanishes on the boundary and satisfies the following differential equation everywhere within the boundary :—

$$\nabla^2 \Omega + t\frac{dt}{dx} - \frac{\sigma x}{1+\sigma} = 0. \quad . \quad . \quad . \quad . \quad (2)$$

In the paper cited a method is given for the approximate determination of Ω when the section of the cylinder is narrow. The limiting form when the width $2t$ is very small is

$$\Omega = \frac{-\sigma x(t^2 - y^2)}{2(1+\sigma)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and equation (1) then becomes

$$\bar{\bar{\chi}} = \frac{(1+3\sigma)\int xt^3 dx}{(1+\sigma)\int t^3 dx}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where, as usual, σ is Poisson's ratio for the material of the cylinder.

An account is given in Part II. of the determination of the position of the flexural centre of a cylinder in the form of a thin aerofoil, and the experimental position

* See Chap. IV. of R. & M. 1444. "Torsion and Flexure of Cylinders and Tubes," by W. J. Duncan.

agrees closely with the theoretical. Experiments were also made on a prism whose section is a narrow isosceles triangle, and although the theory is not strictly applicable to such a beam, yet the formula (4) gives a fair approximation to the truth.

§ 3. *The Centre of Twist.*

Take a cylinder supported in the manner described at the beginning of § 2, and let a couple whose axis is parallel to the generators be applied at the free end. Then there will be a certain point of the terminal section which has zero displacement in the plane of the section *, and this point is called the centre of twist. The location of the centre of twist will depend somewhat on the distribution of the tractions which compose the couple, but the fixing conditions at the root are of greater importance. Again, the definition can be extended to the case where the load is applied and the displacements measured in different sections. Here also the position of the centre will tend to become independent of the choice of the sections for a long cylinder.

Before passing to a detailed discussion of the centre of twist the nature and status of the St. Venant theory of torsion will be briefly considered.

§ 4. *The St. Venant Theory of Torsion.*

St. Venant's theory of torsion resembles his theory of flexure, of which it was the forerunner, in being a special solution of the elastic problem, and, in strictness, of only limited applicability. The importance of the theory arises from its simplicity, and more especially from the fact that the stresses and strains in a long isotropic cylinder under torsional load necessarily approximate closely to those required by the St. Venant theory, except possibly near the places where the loads and constraints are applied. Evidently the stresses and strains in the intermediate portion of the cylinder will be very nearly uniform, *i. e.*, independent of the axial coordinate z. Now it can be shown † that if the curved surface of a cylinder is free from traction, and if the stresses on a normal section are statically equivalent to a pure twisting

* A displacement normal to the section is permitted.

† See Love, 'Mathematical Theory of Elasticity,' 2nd edition, § 237.

couple and are uniform in the above sense, then the stresses and strains are necessarily those given by the St. Venant theory.

In the St. Venant theory of torsion the stresses and strains, and therefore also the torsional stiffness of the cylinder, are quite independent of the choice of the axis of twist. At first sight therefore it would appear as though the axis of twist were actually indeterminate, a conclusion quite at variance with physical intuition. It will be shown in the next section, however, that, provided the boundary conditions are adequately specified, there is no real ambiguity regarding the axis about which the cylinder twists. In the meantime it is proposed to show that the displacement w in the direction of the generators is not independent of the choice of axis of twist.

Take an arbitrary origin O in the section, and let the axis of twist pass through the point T, whose coordinates are (x_T, y_T). Then * the stress function ψ_T is given by

$$\psi_T = \Psi + \tfrac{1}{2}(x-x_T)^2 + \tfrac{1}{2}(y-y_T)^2, \quad . \quad . \quad . \quad (5)$$

where the function Ψ is independent of the choice of the axis of twist. The displacement w_T is given by

$$w_T = \tau\phi_T, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where τ is the twist per unit-length and ϕ_T is the harmonic function conjugate to ψ. Hence

$$\frac{\partial\phi_T}{\partial x} = \frac{\partial\psi_T}{\partial y} = \frac{\partial\Psi}{\partial y} + y - y_T, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and

$$\frac{\partial\phi_T}{\partial y} = -\frac{\partial\psi^T}{\partial x} = -\frac{\partial\Psi}{\partial x} - x + x_T. \quad . \quad . \quad . \quad . \quad (8)$$

Then if ϕ is the value of ϕ_T when T coincides with O, equations (7) and (8) yield on integration

$$\phi_T = \phi - xy_T + yx_T, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and, by (6),

$$w_T = w + \tau(-xy_T + yx_T).$$

* Love, *op. cit.* Chap. XIV. A convenient summary of the formulæ is given in Chap. I. of R. & M. 1444.

§ 5. *Position of the Centre of Twist when the Boundary Conditions are strictly compatible with the St. Venant Theory.*

The expressions for the displacements of a point (x, y, z) of the cylinder are usually given in the form:

$$\left.\begin{aligned} u_{\mathrm{T}} &= -\tau z(y-y_{\mathrm{T}}), \\ v_{\mathrm{T}} &= \tau z(x-x_{\mathrm{T}}), \\ w_{\mathrm{T}} &= \tau\phi_{\mathrm{T}}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

It must be remembered, however, that any rigid body motion can be superposed on these displacements without alteration of the strains and stresses. Accordingly the general expressions are:

$$\left.\begin{aligned} u_{\mathrm{T}} &= -\tau yz + z(\beta' + \tau y_{\mathrm{T}}) - y\gamma' + a, \\ v_{\mathrm{T}} &= \tau xz + x\gamma' - z(\alpha' + \tau x_{\mathrm{T}}) + b, \\ w_{\mathrm{T}} &= \tau\phi + y(\alpha' + \tau x_{\mathrm{T}}) - x(\beta' + \tau y_{\mathrm{T}}) + c, \end{aligned}\right\} \quad . \quad (11)$$

where (a, b, c) is an arbitrary translation, and $(\alpha', \beta', \gamma')$ is an arbitrary small rotation, while the value of ϕ_{T} has been substituted from equation (9).

It has been postulated that the boundary conditions are such that the St. Venant solution is strictly applicable. Accordingly the stresses on the ends of the cylinder are completely determined, and the only element of arbitrariness in the boundary conditions is a kinematical one. Now it is clear from equations (11) that if the boundary conditions are sufficient to render the displacements unique then they fix the values of the following six quantities:—

$$a,\ b,\ c,$$

$$\alpha \equiv \alpha' + \tau x_{\mathrm{T}}, \qquad \beta \equiv \beta' + \tau y_{\mathrm{T}}, \qquad \gamma \equiv \gamma'.$$

Upon substitution of the fixed constants in the equations (11) it is at once evident that the displacements are quite independent of the choice of T, so that this choice has no physical significance *. On the other hand, the coordinates of the centre of twist (as defined in § 3) are immediately found by solution of the simultaneous equations

$$u=0 \quad \text{and} \quad v=0.$$

* In the sequel the suffix T in the displacements will be omitted.

A simple example to illustrate the foregoing argument will now be given. Let the kinematical conditions be as follows :—The origin O is to be fixed, and linear elements at O in the directions OX and OY are to remain fixed in direction.

Since $u=v=w=0$ when $x=y=z=0$, it follows that $a=0$, $b=0$, and $c=-\tau\phi_0$. Next, the displacements v, w of the point $(\delta x, 0, 0)$ must be zero. Hence $\gamma'=0$ and

$$\tau\left\{\phi_0+\left(\frac{\partial\phi}{\partial x}\right)_0\delta x\right\}-\delta x(\beta'+\tau y_T)-\tau\phi_0=0,$$

or

$$\beta'+\tau y_T=\tau\left(\frac{\partial\phi}{\partial x}\right)_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Also the displacements u, w of the point $(0, \delta y, 0)$ must vanish. Hence $\gamma'=0$ as before, and

$$\tau\left\{\phi_0+\left(\frac{\partial\phi}{\partial y}\right)_0\delta y\right\}+\delta y(\alpha'+\tau x_T)-\tau\phi_0=0,$$

or

$$\alpha'+\tau x_T=-\tau\left(\frac{\partial\phi}{\partial y}\right)_0 \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Thus equations (11) become

$$\left.\begin{aligned}\frac{u}{\tau}&=-yz+z\left(\frac{\partial\phi}{\partial x}\right)_0,\\ \frac{v}{\tau}&=xz+z\left(\frac{\partial\phi}{\partial y}\right)_0,\\ \frac{w}{\tau}&=\phi-y\left(\frac{\partial\phi}{\partial y}\right)_0-x\left(\frac{\partial\phi}{\partial x}\right)_0-\phi_0.\end{aligned}\right\} \quad . \quad . \quad (14)$$

Also the centre of twist has the coordinates

$$\left.\begin{aligned}\bar{x}&=-\left(\frac{\partial\phi}{\partial y}\right)_0,\\ \bar{y}&=\left(\frac{\partial\phi}{\partial x}\right)_0.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

§ 6. *Position of the Centre of Twist for Practical Conditions of Support.*

The theoretical method for the determination of the centre of twist given in the last section is of small

practical value, since the conditions of support are seldom strictly compatible with the St. Venant solution, and it is not generally possible to lay down simple kinematical boundary conditions *a priori* *. In practice cylindrical bodies are usually provided with support at one or both ends of the type which may be described as *quasi-rigid*. Here it is not in general possible to say that a particular element of the cylinder will be subject to definite kinematical conditions, for, however nearly the support may approximate to rigidity, there will always be some yield, and the position of the centre of twist will depend in some complicated way on the yields at all parts of the base. A problem of this nature could be investigated precisely if it were possible to solve the mathematical problem of the torsion of a cylinder continuous with a semi-infinite solid of the same material, having a plane face perpendicular to the generators of the cylinder. If the section of the cylinder happens to be symmetrical about a pair of perpendicular axes, and if the torsional load at the free end is symmetrically distributed, then it is clear from symmetry that the centre of twist will be the centroid of the section. This rather trivial case seems to be the only one where the problem has been solved, and the mathematical difficulties appear to be very great when the section has only a single axis of symmetry or is unsymmetrical. However, as will be shown in the next section, the reciprocal theorem provides a means for at least an approximate determination of the centre of twist in the more general cases.

§ 7. *Relation between Flexural Centre and Centre of Twist.*

To simplify the argument suppose at first that the cylinder has completely rigid support at the root, and that the tip is provided with a completely rigid cap to which the loads are applied. Consider the following two systems of load—(*a*) a flexural load applied at the flexural centre, and (*b*) a pure twisting couple—and apply the reciprocal theorem. Under load (*a*) the tip does not twist and the work done by the twisting couple in this displacement is zero; consequently the work done by the flexural load in the displacement produced by the

* This can sometimes be done from considerations of symmetry.

torsional couple must vanish. But the flexural load may have any direction at right angles to the generators, so that its point of application must remain at rest in the torsional displacement. Therefore in this idealized case the centre of twist must coincide with the flexural centre.

Now let the root support be of the quasi-rigid type, *i.e.*, let the cylinder be anchored to a large elastic body whose distant parts can be treated as fixed. There is an apparent difficulty in the application of the reciprocal theorem, because the axial displacements w at the root under torsional load are not now zero, and therefore the flexural stresses at the base may give rise to a finite work-sum in the torsional displacement. However, there is no necessity to apply the reciprocal theorem to the cylinder itself; apply it instead to the body composed of the cylinder and a large hemisphere of the anchoring body, with centre near the base of the cylinder. Then *, if r be the radius of the hemisphere the stresses under any load applied through the cylinder will vary inversely as r^2, and the displacements will vary inversely as r. Consequently any work-sum taken over the hemisphere will vary inversely as r, and will therefore tend to zero as r tends to infinity. Hence it appears that, for the type of support postulated, the work-sum corresponding to the stresses and strains at the root can be neglected.

Next, as regards the tip section, it is evident that, at least for long beams, the general flexural or torsional displacement will be much larger than any local distortions due to the loads. Hence only small errors will be introduced if the tip section be regarded as rigid in the application of the reciprocal theorem.

It may be concluded that for long cylinders provided with quasi-rigid support at the root the centre of twist will be very near to the flexural centre. This conclusion is supported by the experiments described in Part II.

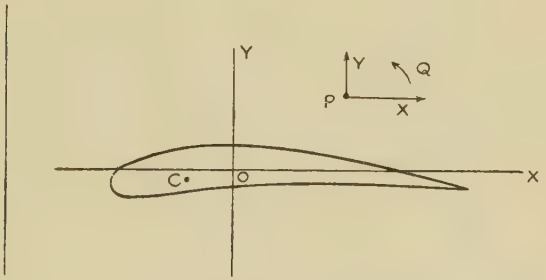
§ 8. *Views of other Writers.*

In the St. Venant theory of torsion the stresses in a cylinder, as well as the torsional stiffness, are independent of the position of the centre of twist. Now in the great majority of practical cases interest is confined to the stresses and the stiffness, and the result has been that

* Love, *op. cit.* §§135, 165.

the question of the location of the centre of twist has received very little attention. Most of those who have considered the point at all have assumed without proof of any kind that the centre of twist is coincident with the centroid of the section. In support of this view it has been contended * that if the axis of twist does not pass through the centroids then bending couples would have to be applied in order to maintain the cylinder in its strained configuration. This is quite true, but, as has been pointed out by Professor Southwell, the curvature of the line of centroids is only of the second order in τ †. Hence the bending stresses, being of the second order, are irrelevant to the question, since the position of the centre of twist is determined by first-order effects.

Fig. 1.



§ 9. *Constrained Torsion.*

Hitherto it has been supposed that the cylinder under consideration is free to move at the tip. When, however, an arbitrary point of the tip section is fixed the influence of a twisting couple is modified by the effects of the reaction at the fixed point. In constrained torsion of this kind the effective torsional stiffness is always higher than in pure (unconstrained) torsion.

Consider a cylinder which is sufficiently long for the local distortions of the tip section to be neglected in comparison with the general displacements due to torsion and flexure. For such a cylinder the centre of twist may be taken to be coincident with the flexural centre. In fig. 1,

* Prescott, 'Applied Elasticity,' § 115.

† When τ is small the expression for the curvature of the helical locus of the centroids is $c\tau^2$, where c is the distance of the centroids from the axis of twist.

O is the centroid of the section and OX, OY are its principal axes ; C is the flexural centre and P the point about which the tip is constrained to rotate.

Let T = torsional stiffness of the unconstrained cylinder,

T′ = torsional stiffness of the constrained cylinder,

F_x = flexural stiffness for load in direction OX,

and F_y = flexural stiffness for load in direction OY.

When a couple Q is applied to the end of the cylinder the constraint at P will cause a reaction with components X and Y. Hence the total twisting moment about C is

$$Q+Y(x_P-x_C)-X(y_P-y_C),$$

and the angle of twist is

$$\theta=\frac{1}{T}\{Q+Y(x_P-x_C)-X(y_P-y_C)\}. \quad . \quad . \quad (16)$$

The forces X and Y are to be determined from the condition that P is to be stationary. Hence

$$\left.\begin{aligned} &\frac{X}{F_x}-\theta(y_P-y_C)=0,\\ \text{and}\quad &\\ &\frac{Y}{F_y}+\theta(x_P-x_C)=0. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

On substitution of the value of θ these equations yield

$$\left.\begin{aligned} &X=\frac{QF_x(y_P-y_C)}{T+F_x(y_P-y_C)^2+F_y(x_P-x_C)^2},\\ \text{and}\quad &\\ &Y=\frac{-QF_Y(x_P-x_C)}{T+F_x(y_P-y_C)^2+F_y(x_P-x_C)^2}. \end{aligned}\right\} \quad . \quad . \quad (18)$$

Hence equation (16) becomes

$$\theta=\frac{Q}{T+F_x(y_P-y_C)^2+F_y(x_P-x_C)^2},$$

or

$$T'=T+F_x(y_P-y_C)^2+F_y(x_P-x_C)^2. \quad . \quad . \quad (19)$$

The torsional stiffness T′ is, of course, a minimum when P coincides with C.

Part II.—Experimental Investigation.

§ 10. *Preliminary.*

Experimental determinations of the position of the flexural centre and centre of twist were made on a mild steel cylinder in the form of an aerofoil of symmetrical section. It was clearly desirable to select a section whose theoretical properties were known, and the one actually adopted was the cubic oval with the equation *

$$\left(\frac{t}{c\theta}\right)^2 = \left(\frac{x}{c}\right)\left(1-\frac{x}{c}\right)^2. \quad . \quad . \quad . \quad . \quad (20)$$

Here x is the abscissa measured from the round nose, c is the chord, t is the upper ordinate or half thickness, and θ is the "thickness parameter." Tests were also made upon a mild steel prism whose section was a slender isosceles triangle. The theory mentioned in § 2 is not applicable to this prism, since the section has sharp angles not lying upon the centre-line; but it was believed that the tests would be of interest as it was anticipated that the centroid and centre of twist would be exceptionally widely separated.

§ 11. *Determination of the Flexural Centre.*

The flexural centre of a cylinder whose section has an axis of symmetry must lie upon that axis. If a constant flexural load in a direction at right angles to the axis of symmetry be applied at a number of points in the section and the twist be measured for each point of application then the position of the flexural centre can be found, since the twist is proportional to the distance of the line of action of the load from that centre. In practice it is inconvenient to traverse the load, but the same result can be obtained by the gradual transfer of load from a scale-pan hanging from one end of the section to a second pan hanging from the other end, the total of the loads remaining constant.

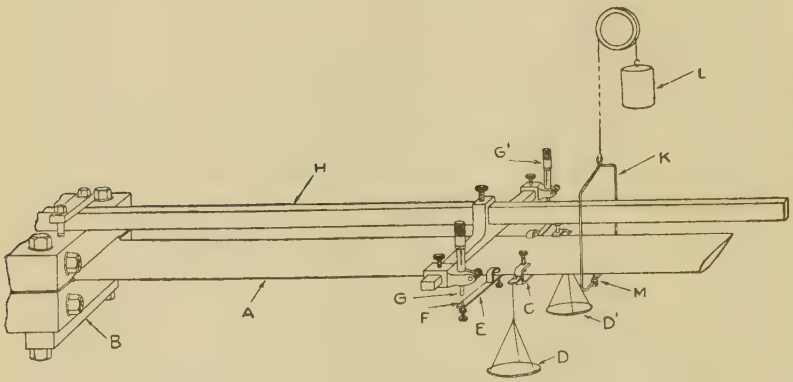
The arrangement of the apparatus actually used is illustrated in fig. 2, where the cylinder of aerofoil section is shown mounted horizontally for test. The cylinder A, which has a chord of 3 inches and an overhang of 3 feet, has a rectangular butt-end which is very securely held by

* See R. & M. 1444, pp. 15 and 67.

the steel clamping blocks B, which in turn are bolted to a massive iron bed-plate. Details of the system of bolts and yokes used to tighten up the clamping blocks can be clearly seen in fig. 3. No square end was provided on the triangular prism, but triangular packing wedges were fitted between the prism and the clamping blocks.

In fig. 2, C is a light steel clamp embracing the cylinder and carrying a pair of scale pans D, D′. The notches from which these pans are suspended lie on the axis of symmetry produced, and the line joining them is set accurately at right angles to the generators of the cylinder. Close to the load bar C is clamped the contact bar E, which carries a pair of sharp-pointed adjustable

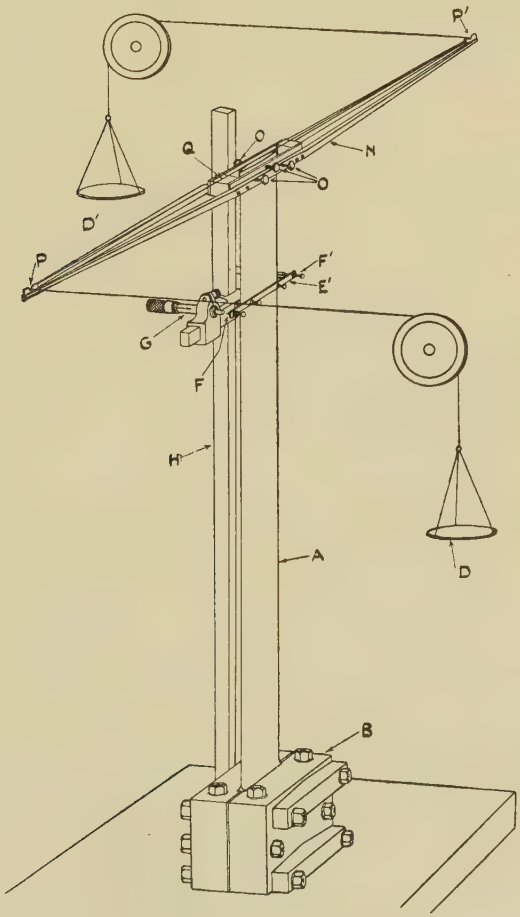
Fig. 2.



contacts F (one of these is hidden in the figure), and immediately above the contacts a pair of micrometer heads G, G′ are mounted. Both micrometers are held in insulating bushes, and matters are arranged so that when the tip of the micrometer spindle touches the contact point a circuit is completed through a suitable indicator. The bracket carrying the micrometers can slide on a bar H which is securely clamped to the base. By means of the counterpoise L and stirrup K a concentrated load is applied to the under surface of the cylinder through a screw M, whose pointed end presses on a small brass pad in contact with the surface. This load, which is kept constant during an experiment, serves to neutralize the sag of the cylinder under its own weight. The only error which could be introduced by this counterpoise would be

due to variation of the friction on the pulley spindle, but any such error is minimized by applying the load as nearly as possible at the flexural centre.

Fig. 3.



As a preliminary to a measurement the contact points F are adjusted to lie on the axis of symmetry produced, and the line joining them is set at right angles to the generators with all possible accuracy *. Readings of the micrometers G, G′ are taken with the scale pans empty,

* If this precaution is neglected the results obtained will be quite erroneous. See § 14.

and then a suitable load is placed in the pan D and the micrometers again read. The load is transferred to D′ in steps, and the micrometers are read at each stage. In this way the twist corresponding to each position of the resultant load is found. Finally, the twist is plotted against the abscissa of the resultant load, and the flexural centre found as the point for which the twist is zero.

§ 12. *Determination of the Centre of Twist.*

For the determination of the centre of twist the cylinder was mounted vertically, as shown in fig. 3. The method of clamping the cylinder and the arrangement of the contacts and micrometers were the same as in the flexural tests, but here the load consisted of a pure torsional couple applied by the torque bar N. This bar was built from light aluminium angles, and was clamped to the free end of the cylinder by six screws O, which permitted adjustment in any direction. The threads by which load was applied to the torque bar passed through notches in the bar, and rested at the bottom of the notches on a taut wire stretched between P and P′. When the cylinder has been set vertical and the wire PP′ horizontal it is clear that the application of equal and opposite horizontal forces at P and P′ will produce a pure torsional couple on the cylinder *. The horizontal threads were passed over pulleys whose bearings were made as nearly frictionless as possible, and were connected to the scale-pans D, D′.

The procedure in an experiment consists in measuring the displacements of F and F′ for a series of equal loads in the scale-pans. In each complete set of tests the measurements were repeated with the pulleys interchanged in order to correct for possible differences in their frictional coefficients, and then another similar set of measurements was made with the direction of twist reversed. Finally, the displacements were plotted against the torque, and the best straight lines fitted by the "zero-sum" method. The position of the centre of twist is immediately found from the mean ratio of the displacements of F and F′.

* See § 14 regarding the nature of the errors introduced when PP′ is not perpendicular to the generators.

§ 13. *Measurement of the Elastic Constants of the Steel.*

A knowledge of the value of Poisson's ratio σ is required in order to apply the theoretical formula for the position of the flexural centre, and σ can only be found from the values of Young's modulus E and the rigidity modulus μ. The cylinder and prism used in the main experiments were machined from bars of normalized mild steel belonging to a single batch, and the materials were presumed to be identical. A tensile test piece was cut from one of the bars and tested in the Engineering Department of the National Physical Laboratory. The result of the test as given in the report is

$$E = (30{\cdot}02 \pm 0{\cdot}15) \times 10^6 \text{ lb. per sq. in.},$$

and the value 30×10^6 will be adopted. Values of μ can be deduced from the results of the torsional tests on the cylinder and prism, but as these were of unorthodox sectional form it was considered desirable to have an independent determination. The steel bars were too slender to provide a test piece suitable for the existing torsional testing machine in the Engineering Department, so that a special test had to be devised. In order to obtain large torsional displacements with small loads and stresses it was necessary to use a long specimen, and the accurate maching of a long and very slender circular test piece was impracticable. Accordingly a square section was adopted, and the specimen, which was 12″ long and 0·2″ thick, was machined with ease and accuracy on a surface grinder provided with a magnetic chuck. In the tests the square prism was clamped at its upper end in a vertical position. The torque was applied at the lower end by means of a torque bar, and the twist was measured by contact bar and micrometers all very much in the manner described in § 12. In order to avoid possible errors due to constraints at the ends the twist was measured at two different positions, neither of which lay within four diameters of the clamp, and the stiffness was deduced from the difference of the measured displacements. The mean result of several measurements was $\mu = 11{\cdot}86 \times 10^6$ lb. per sq. in., and similar tests on a square prism cut from the outer end of the oval sectioned

cylinder gave $\mu = 11{\cdot}74 \times 10^6$. The value adopted for μ is $11{\cdot}8 \times 10^6$, and consequently

$$\sigma = \frac{E}{2\mu} - 1 = \frac{30}{23{\cdot}6} - 1 = 0{\cdot}27.$$

§ 14. *Errors due to Incorrect Setting of the Apparatus.*

The experimental methods for the determination of the flexural centre and centre of twist are extremely simple in principle, but experience shows that great care is required in setting up the apparatus if serious errors are to be avoided. The need for special care arises, broadly, from the fact that the flexural displacements produced by an isolated load applied directly to the surface of a long cylinder are, in general, very much greater than the torsional displacements.

Consider first the flexural tests (see fig. 2). When the apparatus is correctly set up the contacts F and F′ are situated at the same distance z from the base. But suppose that the actual distances are $(z \pm e)$. Then by the usual formula for the deflexion of a cantilever beam the difference δy in the flexural displacements of the contacts is given by

$$\delta y = \frac{W}{EI}\left[\tfrac{1}{2}l\{(z+e)^2 - (z-e)^2\} - \tfrac{1}{6}\{(z+e)^3 - (z-e)^3\}\right],$$

where W = flexural load,

l = distance of point of application of the load from the root,

and EI = flexural rigidity of the cylinder.

When this expression is expanded and e^3 neglected it becomes

$$\delta y = \frac{Wez(2l-z)}{EI} \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Let D be the distance between the contacts F. Then the difference in displacement δy corresponds to an apparent twist

$$\delta\theta = \frac{Wez(2l-z)}{DEI} \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

In order to neutralize this spurious twist the load W

would have to be moved from the true flexural centre by a distance δx given by

$$\delta x = \frac{C.\delta\theta}{Wz} = \left(\frac{C}{EI}\right)\frac{e(2l-z)}{D}, \quad . \quad . \quad . \quad (23)$$

where C is the torsional stiffness of unit length of the cylinder. It will be seen that the importance of the correction increases with the span of the cylinder.

Next, consider the torsional experiment (see fig. 3), and suppose that the contacts F, F′ are at distances d, $(D-d)$ from the true centre of twist. Let the displacements be y and y'. Then $y=\theta d$ and $y'=\theta(D-d)$,

so that

$$d = \frac{Dy}{y-y'}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Let PP′=S, and suppose that through an error in setting P is a distance h above P′. Then the couple SW due to the tensions in the threads has its axis inclined to the generators of the cylinder at the small angle h/S. Consequently the couple has a component which tends to bend the cylinder at right angles to the plane of symmetry and of magnitude hW. The displacement due to this couple is

$$\delta y = \frac{hWz^2}{2EI}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Consequently, by (24), the centre of twist is apparently at the distance $(d+\delta d)$ from F, where

$$\delta d = \frac{D\delta y}{y-y'}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

But

$$y-y' = D\theta = \frac{DSWz}{C}.$$

Hence (25) and (26) yield

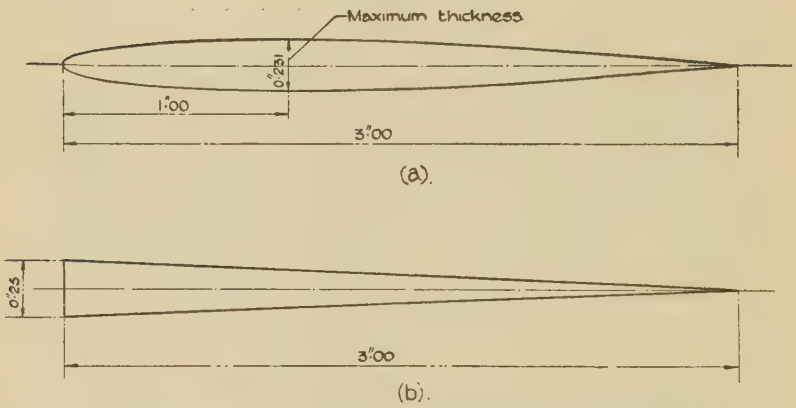
$$\delta d = \left(\frac{C}{EI}\right)\frac{hz}{2S}. \quad . \quad . \quad . \quad . \quad . \quad (27)$$

A further error arises in the flexural experiment if the loading threads are not at the same distance from the base, and in the torsional experiment if the contacts F, F′ are not at the same distance from the base. These errors can be investigated on the lines already indicated.

§ 15. *Experiments on a Cylinder of Oval Section.*

The theoretical form of the section is the cubic oval given by equation (20) with $c = 3$ inches and $\theta = 0{\cdot}1$. This section is shown accurately drawn in fig. 4(*a*). As the maximum thickness is only 0·231 inch and the length of the cylinder (excluding the rectangular butt-end) is 36·6 inches, it will readily be appreciated that the machining of the cylinder presented a problem of great difficulty. However, a suitable method was evolved, and it will be seen from Table I. that the actual section approximates closely to the theoretical form. The differences are not com-

Fig. 4.



pletely negligible, and have been allowed for in the comparisons between theory and experiment.

A description of the experimental methods has been given in §§ 11 and 12, and it only remains to add that the chief source of difficulty in the attainment of accurate micrometer readings was the vibration of the building in which the experiments were conducted. Specimen sets of observations with appended reductions are given in Tables II. and III., and the same observations are shown plotted in figs. 5 and 6. The smallness of the differences of the micrometer readings in Table III. illustrates the difficulty of obtaining accuracy in the determination of the flexural centre. A complete summary of the measurements of the flexural and torsional centres is given in Table IV., and it will be seen that the two centres are

TABLE I.—Dimensions of Cylinder of Aerofoil Section.
Length=36·6 in.; Chord=3·0 in.
Thicknesses measured at five sections $8\frac{5}{8}$ inches apart.

Distance from leading edge.	Mean thickness as measured.	Theoretical thickness.
in.	in.	in.
0	0	0
0·01	0·035	0·034
0·02	0·048	0·049
0·03	0·062	0·059
0·04	0·072	0·069
0·05	0·079	0·076
0·06	0·085	0·083
0·07	0·092	0·089
0·08	0·098	0·096
0·09	0·103	0·101
0·10	0·108	0·106
0·2	0·147	0·145
0·25	0·159	0·159
0·3	0·172	0·171
0·4	0·190	0·190
0·5	0·202	0·204
0·6	0·212	0·215
0·75	0·223	0·225
0·8	0·225	0·227
1·0	0·232	0·231
1·25	0·227	0·226
1·5	0·215	0·212
1·75	0·193	0·191
2·0	0·165	0·163
2·25	0·133	0·130
2·5	0·095	0·091
2·75	0·053	0·048
3·0	0	0

very nearly coincident; it is doubtful if any of the differences, except possibly for the position at 6 inches from the root, exceed the experimental errors.

TABLE II.—Torsion of Cylinder of Aerofoil Section.

Deflexions measured 17″ from base.
Distance between contacts=4·01″.
Distance of leading edge contact from leading edge=0·42″.
Torque applied at free end of cylinder, a positive load indicating anticlockwise torque, and negative clockwise.
Weight of each scale-pan=20·0 gm. Arm of couple 3 ft.

Total load.	Micrometer readings.					
	Leading edge micrometer.	Leading edge micrometer with pulleys interchanged.	Mean.	Trailing edge micrometer.	Trailing edge micrometer with pulleys interchanged.	Mean.
gram.	in.	in.	in.	in.	in.	in.
520	0·3612	0·3611	0·3612	0·4208	0·4208	0·4208
420	0·3644	0·3643	0·3644	0·4165	0·4166	0·4166
320	0·3671	0·3669	0·3670	0·4120	0·4119	0·4120
220	0·3700	0·3700	0·3700	0·4078	0·4076	0·4077
120	0·3728	0·3728	0·3728	0·4033	0·4032	0·4033
20	0·3757	0·3757	0·3757	0·3989	0·3989	0·3989
− 20	0·3769	0·3767	0·3768	0·3970	0·3970	0·3970
−120	0·3794	0·3794	0·3794	0·3926	0·3927	0·3927
−220	0·3824	0·3822	0·3823	0·3880	0·3885	0·3883
−320	0·3848	0·3849	0·3849	0·3835	0·3835	0·3835
−420	0·3877	0·3880	0·3879	0·3792	0·3793	0·3793
−520	0·3908	0·3909	0·3909	0·3750	0·3749	0·3750

The straight lines which fit these observations best, as found by the "zero-sum" method, have the following slopes:

Leading edge $=2{\cdot}812\times10^{-5}$ in. per gm.
Trailing edge $=4{\cdot}431\times10^{-5}$ „

Hence distance of centre of twist from leading edge $=\left(4{\cdot}01\times\frac{2{\cdot}812}{2{\cdot}812+4{\cdot}431}\right)-0{\cdot}42$

$=1{\cdot}437$ inches or 0·379 chord.

TABLE III.—Flexure of Cylinder of Aerofoil Section.

Flexure measured 17″ from base; load at 19″.

Distance between contacts=7·92″.

Distance between loading threads=3·76″.

Distance of leading edge thread from leading edge=0·38″.

Constant sum of loads=2500 grams.

Difference columns give the differences of the deflexions at the leading edge and trailing edge contacts.

Load in leading edge pan.	Leading edge deflexion less trailing edge deflexion.	Leading edge deflexion less trailing edge deflexion, with prism reversed.
gm.	in.	in.
0	−0·0222	−0·0225
250	−0·0184	−0·0188
500	−0·0147	−0·0151
750	−0·0110	−0·0110
1000	−0·0072	−0·0077
1250	−0·0033	−0·0038
1500	+0·0002	+0·0009
1750	0·0039	0·0039
2000	0·0077	0·0081
2250	0·0116	0·0118
2500	0·0154	0·0153

The load corresponding to zero difference in deflexion is given by the "zero-sum" method to be 1480 gm. in leading edge pan for both the original and the reversed positions. Hence distance of flexural centre from leading edge

$$=\left(3{\cdot}76\times\frac{2500-1480}{2500}\right)-0{\cdot}38$$

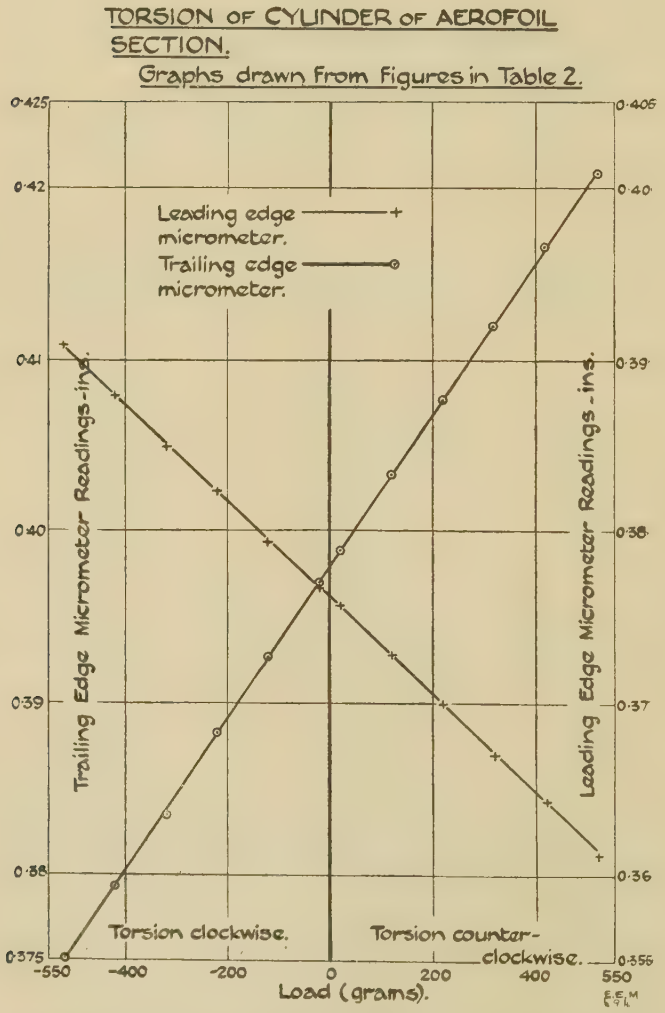
$$=1{\cdot}15''\text{ or }0{\cdot}383\text{ chord.}$$

The theoretical position of the flexural centre may be found from equation (316) of R. & M. 1444. This equation

states that the distance $\bar{\bar{\chi}}$ of the flexural centre aft of the centroid of the section is given by

$$\bar{\bar{\chi}} = -\frac{4c}{91(1+\sigma)}\left\{1+3\sigma-6\sigma\theta^2+\frac{(202\sigma-56)\theta^4}{17}\right\}. \quad (28)$$

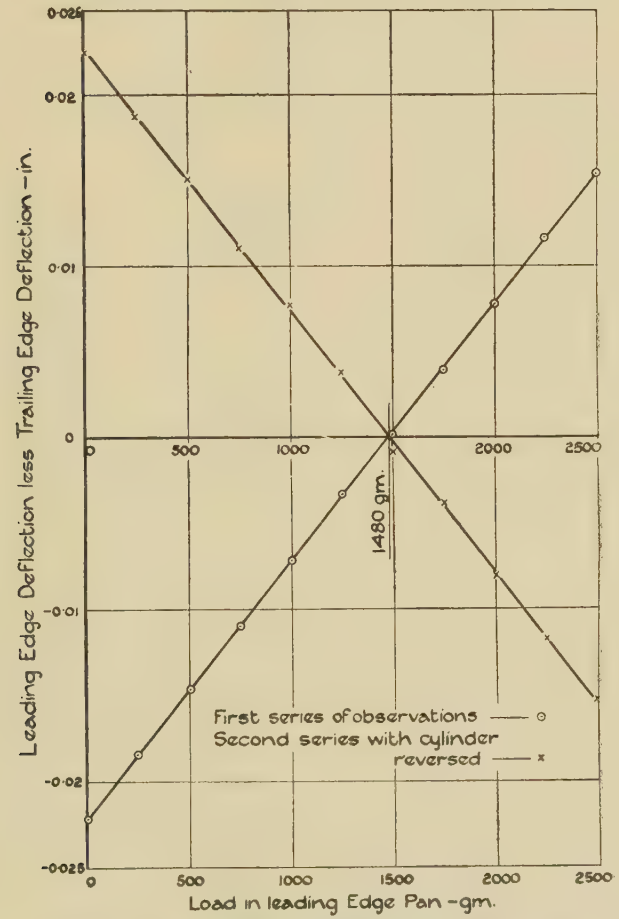
Fig. 5.



Since the actual section deviates somewhat from the theoretical, it has been necessary to correct the calculated position of the flexural centre. This has been done on the

assumption that the ratio of the distance of the flexural centre from the centroid to the distance of the centroid of the cubed ordinates from the centroid is the same for

Fig. 6.



Flexure of Cylinder of Aerofoil Section Graph drawn from figures in Table 3. Note that to avoid confusion the signs for the reversed position have been changed.

the actual and theoretical sections (see equation (4)). As the correction is small the method can hardly be appreciably in error. In order to find the centroid and the centroid of the cubed ordinates for the actual section it

TABLE IV.—Summary of Observations for Cylinder of Aerofoil Section.
Positions of centres given as fractions of chord from leading edge.

Part of cylinder observed.	Distances of centres from leading edge.				Flexural load and point of application.
	Torsional.	Flexural.	Flexural with prism reversed.	Mean flexural.	
Base to 28″	0·373 chord.	0·367 chord.	0·383 chord.	0·375 chord.	1500 gm. at 30″.
Base to 28″: 1st Repeat.....	0·377 ,,	—	—	—	,, ,,
Base to 28″: 2nd Repeat	0·373 ,,	—	—	—	,, ,,
Base to 17″	0·379 ,,	0·383 chord.	0·383 chord.	0·383 chord.	2500 gm. at 19″.
Base to 6″	0·387 ,,	0·407 ,,	0·417 ,,	0·412 ,,	2500 gm. at 8″.
Base to 3″	—	0·403 ,,	0·400 ,,	0·402 ,,	2500 gm. at $3\frac{3}{4}$″.
*Between 6″ and 28″..	0·370 ,,	0·367 ,,	0·374 ,,	0·371 ,,	—
*Between 6″ and 17″..	0·375 ,,	0·347 ,,	0·374 ,,	0·361 ,,	—

* By difference.

Apparent position of torsional centre with load bar deliberately mis-set, the load points being at $\pm 0{\cdot}05$″ from the mean position :

Part of cylinder observed.	Distance of torsional centre from leading edge.
Base to 28″.....	0·427 chord.
Base to 6″	0·401 ,,

has been necessary to employ Simpson's rule. A check on the accuracy of the rule in its application to the measured ordinates has been obtained by applying it to a corresponding set of theoretical ordinates, and comparison of the results with the true value of the integrals. As shown in Table V. the rule is completely accurate. The final

TABLE V.—Summary of Calculations for Flexural Centre of Cylinder.

Quantity or expression.	From measured ordinates, by Simpson's Rule.	Theoretical section.	
		Exact value by integration.	From theoretical ordinates by Simpson's Rule.
Area $= \int_0^c 2t\,dx$	0·4848	0·4800	0·4800
First moment $= \int_0^c 2t\,x\,dx$	0·6282	0·6171	0·6171
Distance of centroid from leading edge	1·296″ =0·432 chord	1·286″ =0·429 chord	1·286″ =0·429 chord
$\int_0^c (2t)^3\,dx$	$18{\cdot}16 \times 10^{-3}$	$17{\cdot}953 \times 10^{-3}$	$17{\cdot}953 \times 10^{-3}$
$\int_0^c (2t)^3\,x\,dx$	$21{\cdot}20 \times 10^{-3}$	$20{\cdot}715 \times 10^{-3}$	$20{\cdot}712 \times 10^{-3}$
Distance of centroid of cubed ordinates from leading edge	1·168″ =0·389 chord	1·154″ =0·385 chord	1·154″ =0·385 chord
Distance of centroid of cubed ordinates from centroid	0·128″ =0·043 chord	0·132″ =0·044 chord	0·132″ =0·044 chord
Distance of calculated position of flexural centre from leading edge (assumed $\sigma=0{\cdot}27$)	1·115″ =0·373 chord	1·100″ =0·367 chord	1·100″ =0·367 chord

result of the calculations is that the flexural centre is at a distance of 0·372 of the chord from the leading edge. It will be seen from Table IV. that for the portion of the cylinder between 28 inches and 6 inches from the base the distances of the flexural and torsional centres in chords from the leading edge were 0·371 and 0·370 respectively, so that there is good agreement between theory and experiment.

The torsional experiments incidentally provided measurements of the torsional stiffness of the cylinder. It is shown on p. 18 of R. & M. 1444 that an approximation to the stiffness of unit length of a cylinder whose section is defined by equation (20) is

$$C_{10}=\frac{256\mu c^4\theta^3}{3465}\left(1-\frac{11}{13}\theta^2+\theta^4-\frac{379}{221}\theta^6\right). \quad . \quad (29)$$

This expression is obtained by the reduction of the integral

$$C_{10}=2\mu\iint\Psi_9\,dx\,dy, \quad . \quad . \quad . \quad . \quad . \quad (30)$$

where Ψ_9 is a particular approximation to the shearing stress function Ψ. Now it is shown in the place cited that

$$(1-292\theta^8)\Psi\leqq\Psi_9\leqq(1+27{\cdot}68\theta^8)\Psi. \quad . \quad . \quad (31)$$

TABLE VI.—Torsional Stiffness of Cylinder of Aerofoil Section.

Portion of cylinder tested.	Stiffness ; lb. in. per radian for 1″ length.
Base to 6″	$7{\cdot}84\times10^4$
Base to 17″	$7{\cdot}47\times10^4$
Base to 28″	$7{\cdot}43\times10^4$
*Between 6″ and 17″.....	$7{\cdot}28\times10^4$
*Between 6″ and 28″.....	$7{\cdot}33\times10^4$
*Between 17″ and 28″	$7{\cdot}37\times10^4$

* By difference.

Hence, if C is the true value of the stiffness, it follows from (30) that

$$(1-292\theta^8)C\leqq C_{10}\leqq(1+27{\cdot}68\theta^8)C. \quad . \quad . \quad (32)$$

In the present instance $\theta=0{\cdot}1$, and the inequality becomes

$$0{\cdot}99999808\,C\leqq C_{10}\leqq 1{\cdot}0000002768\,C. \quad . \quad . \quad (33)$$

Hence the theoretical error in C_{10} is utterly negligible. The formula (29), however, requires correction on account of the deviation of the actual section of the cylinder from the theoretical form. This has been done on the assumption that the actual and theoretical stiffnesses are proportional to the respective values of the integral of the cubed ordinates (see Table V.).

The results of the measurements of the torsional stiffness are given in Table VI., from which it will be seen that the part of the cylinder near the base was appreciably stiffer than the remainder. This must be attributed to the constraint due to the clamping at the base. By use of equation (29), corrected as already explained, the following values of the rigidity modulus have been obtained :—

For portion of cylinder between

6″ and 17″, $\mu = 12{\cdot}17 \times 10^6$ lb. in.$^{-2}$.
17″ and 28″, $\mu = 12{\cdot}32 \times 10^6$,,
6″ and 28″, $\mu = 12{\cdot}24 \times 10^6$,,

Another test on the portion between 6″ and 24″ gave $\mu = 12{\cdot}19 \times 10^6$. These values of μ are appreciably higher than the value $11{\cdot}8 \times 10^6$ obtained from the tests on the small square prisms. The discrepancy appears to exceed the possible experimental error, and has not as yet been explained.

§ 16. *Experiments on an Isosceles Triangular Prism.*

The section of the prism is a slender isosceles triangle, and is illustrated in fig. 4(*b*). Careful measurements of the section were made at five evenly spaced positions, and the mean results are given in Table VII. For the purpose of comparison with theory the triangle which fits the measurements best was found by the "zero-sum" method and used in place of the actual section. This mean triangle has the dimensions :—

Altitude .... 3·023 inches.
Base ..... 0·2476 inch.

A summary of the results of the determinations of the flexural and torsional centres is given in Table VIII. It will be seen that both the centres lie very near to the base. The two centres are apparently not quite coincident, as the torsional centre is found to lie consistently nearer to the base by about 0·03 of the chord. Although, as pointed out in § 10, the formula (4) is not strictly applicable to the prism, it has been thought interesting to calculate the position of the flexural centre from the formula. With $\sigma = 0{\cdot}27$ the result is that the distance from the base to the flexural centre is 0·143 of the altitude. The measured positions of the centres do not

deviate far from this except for the part of the prism very near to the root.

TABLE VII.—Dimensions of Triangular Prism.

Each figure is the mean of five measurements taken at equal intervals along the length of the prism.

Distance from blunt edge.	Mean thickness.
in.	in.
0	0·2450
0·25	0·2280
0·5	0·2073
0·75	0·1868
1·0	0·1660
1·25	0·1454
1·5	0·1247
1·75	0·1040
2·0	0·0835
2·25	0·0631
2·5	0·0429
2·75	0·0230

TABLE VIII.—Summary of Observations on Prism of Triangular Section.

Positions of centres given as fractions of the altitude measured from the base.

Part of prism observed.	Distances of centres from base as fraction of chord.				Flexural load.
	Torsional.	Flexural.	Flexural with prism reversed.	Mean flexural.	
Root to 28″	0·127	0·144	0·153	0·151	1000 gm. at 30″
Root to 28″ Repeat	—	—	0·157		
Root to 17″	0·137	0·165	0·173	0·169	2000 gm. at 19″
Root to 6″	0·147	0·187	0·187	0·187	2500 gm. at 8″
Root to 3″	0·146	0·168	0·181	0·174	2500 gm. at 3¾″
*Between 6″ and 28″.....	0·119	0·137	0·150	0·143	—
*Between 6″ and 17″.....	0·131	0·160	0·167	0·163	—

* By difference.

The mean torsional stiffness of 1 inch length of the prism for the portion lying between 28 inches and 6 inches from the root was found to be $4{\cdot}12\times10^4$ lb. in. per radian. An accurate theoretical expression for the stiffness of an isosceles triangular prism is not known, but it is shown in the Appendix that a good approximation* can be obtained by the aid of Ritz's method. The formula is (see equation (18) of the Appendix)

$$C=\frac{2\mu m^3c^4}{3(1-m^2)}\left(1-\frac{4}{r+4}\right), \quad . \quad . \quad . \quad (34)$$

where

$$m=\tan\frac{\alpha}{2},$$

α=vertical angle of the triangle,

c=altitude of the triangle,

and

$$r=\frac{\sqrt{6m^2+10}}{2m}-2, \quad . \quad . \quad . \quad . \quad (35)$$

or, very nearly,

$$r=\frac{\pi}{\alpha}-2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

On application of equation (34) it is found that $\mu=11{\cdot}95\times10^6$ lb./sq. in., and this is in fair agreement with the value $11{\cdot}8\times10^6$ obtained from the tests on the square prisms.

Appendix.

Approximate Solution of the St. Venant Torsion Problem for an Isosceles Triangular Prism.

So far as the writers are aware no exact solution of the problem has yet been found when the vertical angle of the triangular section is general. However, a simple approximate solution, which is sufficiently accurate for most practical purposes, can be obtained by means of Ritz's method†. Let Ψ be the torsional stress function for the section‡. Then the integral

$$U=\iint\left\{\tfrac{1}{2}\left(\frac{\partial\Psi}{\partial x}\right)^2+\tfrac{1}{2}\left(\frac{\partial\Psi}{\partial y}\right)^2-2\Psi\right\}dx\,dy \quad . \quad (1)$$

* The expression is exact for the equilateral triangle, and the fractional error tends to vanish as the vertical angle of the triangle tends to zero.

† See the Appendix to Chap. I. of R. & M. 1444.

‡ Love, *loc. cit.*, or R. & M. 1444, Chap. I.

is stationary for small variations of Ψ which vanish on the boundary. In the application of this theorem a function Ψ which vanishes on the boundary and contains a number of disposable parameters or functions is chosen, and the parameters or functions are determined so as to render U stationary.

Suppose that the section of the wedge is bounded by the three straight lines

$$y=\pm mx, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$x=c. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Then, as can be verified at once, the exact solution of the problem when c is infinite is

$$\Psi_\infty = \frac{m^2x^2-y^2}{1-m^2}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Assume then that for the finite wedge

$$\Psi = \frac{m^2x^2-y^2}{1-m^2} f(x), \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $f(c)$ is zero. Accordingly

$$(1-m^2)\frac{\partial \Psi}{\partial x} = 2m^2xf(x)+(m^2x^2-y^2)f'(x),$$

and

$$(1-m^2)\frac{\partial \Psi}{\partial y} = -2yf(x).$$

Hence the integrand of U, when multiplied by $(1-m^2)^2$, becomes

$$2m^4x^2f(x)^2+2m^2x(m^2x^2-y^2)f(x)f'(x)$$
$$+\tfrac{1}{2}(m^2x^2-y^2)^2f'(x)^2+2y^2f(x)^2-2(1-m^2)(m^2x^2-y^2)f(x),$$

and if the variation of $f(x)$ is δ, then the variation of the last expression is

$$\Delta \equiv \delta \left\{ \begin{array}{l} 4m^4x^2f(x)+2m^2x(m^2x^2-y^2)f'(x) \\ \quad +4y^2f(x)-2(1-m^2)(m^2x^2-y^2) \end{array} \right\}$$
$$+\frac{d\delta}{dx}\{2m^2x(m^2x^2-y^2)f(x)+(m^2x^2-y^2)^2f'(x)\}. \quad (6)$$

The function $f(x)$ must be determined so as to satisfy the equation

$$\int_0^c \int_{-mx}^{+mx} \Delta \, dx\, dy = 0. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Perform the integration with respect to y, and note that

$$\int_{-mx}^{+mx} y^2 dy = \frac{2}{3} m^3 x^3,$$

$$\int_{-mx}^{+mx} (m^2x^2 - y^2)\, dy = \frac{4}{3} m^3 x^3,$$

and

$$\int_{-mx}^{+mx} (m^2x^2 - y^2)^2\, dy = \frac{16}{15} m^5 x^5.$$

Then

$$\int_0^c \int_{-mx}^{+mx} \Delta \, dx\, dy = \int_0^c \mathrm{X}\, dx, \quad . \quad . \quad . \quad (8)$$

where

$$\mathrm{X} = \frac{8}{3} m^3 x^3 \delta \{(3m^2+1) f(x) + m^2 x f'(x) - (1-m^2)\}$$

$$+ \frac{8}{15} m^5 x^4 \frac{d\delta}{dx} \{5f(x) + 2x f'(x)\}. \quad . \quad . \quad . \quad (9)$$

On integration by parts

$$\int_0^c \frac{d\delta}{dx} \{5x^4 f(x) + 2x^5 f'(x)\} dx = \Big[5x^4 f(x)\delta + 2x^5 f'(x)\delta \Big]_0^c$$

$$- \int_0^c \delta \{20x^3 f(x) + 15x^4 f'(x) + 2x^5 f''(x)\} dx,$$

and the term in square brackets vanishes, since, by hypothesis, δ vanishes at the upper limit. Hence equation (7) becomes

$$\frac{8m^3}{15} \int_0^c x^3 \{2m^2x^2 f''(x) + 10m^2 x f'(x) - 5(1-m^2) f(x)$$

$$+ 5(1-m^2)\} \delta \, dx = 0.$$

By the usual argument of the calculus of variations the coefficient of δ in the integrand must vanish. Hence $f(x)$ must satisfy the differential equation

$$2m^2x^2 f''(x) + 10m^2 x f'(x) + 5(1-m^2)(1-f(x)) = 0. \quad (10)$$

This equation obviously has the particular integral $f(x) = 1$. Put

$$f(x) = 1 + ax^n. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Then (10) is satisfied if

$$n = -2 \pm \frac{\sqrt{6m^2+10}}{2m}.$$

But $f(x)$ clearly must not become infinite, so that the radical must be taken with the positive sign. Also $f(c)$ must vanish. Hence

$$f(x)=1-\left(\frac{x}{c}\right)^r, \quad \ldots\ldots \quad (12)$$

where

$$r=\frac{\sqrt{6m^2+10}}{2m}-2. \quad \ldots\ldots \quad (13)$$

Finally, the approximate stress function is

$$\Psi=\frac{m^2x^2-y^2}{1-m^2}\left(1-\left(\frac{x}{c}\right)^r\right). \quad \ldots\ldots \quad (14)$$

Some values of m, r, and $\alpha\equiv 2\arctan m$ are given in the following table, from which it will be seen that r is very nearly equal to r', where

$$r'=\frac{\pi}{\alpha}-2. \quad \ldots\ldots \quad (15)$$

Value of r.	Value of m.	Vertical angle of triangle $=\alpha$.
0	1·0	90°
1·0	$1/\sqrt{3}$	60°
2·0	$1/\sqrt{5·8}$	45° 6′
3·0	$1/\sqrt{9·4}$	36° 8′
4·0	$1/\sqrt{13·8}$	30° 8′
5·0	$1/\sqrt{19}$	25° 52′
6·0	0·2	22° 37′
$\frac{\sqrt{10}}{2m}-2$ approx.	Small.	$2m$ (radians) approx.

If Ψ had been exact it would have satisfied the differential equation

$$\nabla^2\Psi+2=0, \quad \ldots\ldots \quad (16)$$

but when Ψ has the value (14) it is found that

$$\nabla^2\Psi+2=\frac{(x/c)^r}{1-m^2}\left\{2-m^2(r^2+3r+2)+r(r-1)\frac{y^2}{x^2}\right\}. \quad (17)$$

The greatest value of y^2/x^2 is m^2 and the least value is 0, so that the extreme values of the bracketed expression are $2-m^2(4r+2)$ and $2-m^2(r^2+3r+2)$. When $m=1/\sqrt{3}$

and $r=1$ these extreme values are both zero, so that the expression (14) is exact for the equilateral triangle. For a narrow wedge r is large, $(x/c)^r$ is small except near the base, and the approximation is accordingly very good except quite near to the base.

The formula for the torsional stiffness of unit length of the cylinder is

$$C=2\mu\iint\Psi\,dx\,dy$$

$$=\frac{2\mu m^3c^4}{3(1-m^2)}\left(1-\frac{4}{r+4}\right). \quad . \quad . \quad . \quad . \quad (18)$$

This expression is almost certainly amply accurate for practical requirements, as it is a characteristic of Ritz's method that it gives a much better approximation to the stiffness than to the stresses themselves.

Two limiting forms of the expression (14) may be noted. In the first place, when m is very small r becomes very large, and in the limit

$$\Psi=(m^2x^2-y^2)\left(1-e^{-\frac{\sqrt{10}}{2ma}(a-x)}\right). \quad . \quad . \quad (19)$$

Also, when the vertical angle is a right angle $m=1$, $r=0$, and the right-hand side of (14) assumes the indeterminate form 0/0. However, it can be shown without difficulty that the limiting form is

$$\Psi=\frac{5}{8}(x^2-y^2)\log\left(\frac{c}{x}\right). \quad . \quad . \quad . \quad . \quad (20)$$

XVI. *On Musical Air-Bubbles and the Sounds of Running Water.* *By* M. Minnaert, *Sc.D., Heliophysical Institute of the Physical Laboratory, Utrecht* *.

PHYSICISTS have hardly ever investigated the sounds of running water. As a matter of fact we know very little about the murmur of the brook, the roar of the cataract, or the humming of the sea. It is in conformity with the essence of the physical method that we should begin by reducing such acoustical complexes to much simpler elementary phenomena.

* Communicated by Prof. L. S. Ornstein.

In the interesting popular book of Sir W. Bragg on sound we read that Sir Richard Paget has investigated the sounds which originate when single drops fall into a vessel filled with water *. He found that each drop makes a small cavity in the water, which then closes, and gives a sound much like a resonator with rigid walls.

I had already tried, some years ago †, to investigate the sounds of running water in an entirely different way, viz., by letting air escape in bubbles from the orifice of a tube immersed in water; each bubble gives a sound of very definite pitch. For this particular phenomenon I had conceived quite another explanation than that of Sir R. Paget, and the experiments which I made after reading his work have only corroborated my first view.

For the present it seems probable that the kind of vibration is not the same in the cases investigated by Sir R. Paget and by me, and that the sounds of running water originate in at least two different ways.

1. *Experimental Method.*

The apparatus used is very simple and consists of a funnel A, from which the water slowly streams through the tube BC, and gradually ascends in the wider tube CD. The air is displaced and escapes through the tube DE, of which the end, immersed in the midst of a pail filled with water, is curved upwards and carries a tapering terminal tube made of brass or glass; several terminal tubes of different diameters are interchangeable. The velocity of the air current is extremely reduced by the pinchcock placed in C, or at any place of the tube where there is water flowing; where air passes a good regulation is impossible.

Already the first experiments showed that the sound originates at the moment when the bubble closes at the end of the terminal tube, and not when it emerges and bursts at the surface (as many people would think) ‡. With some precautions it is fairly easy to prevent water

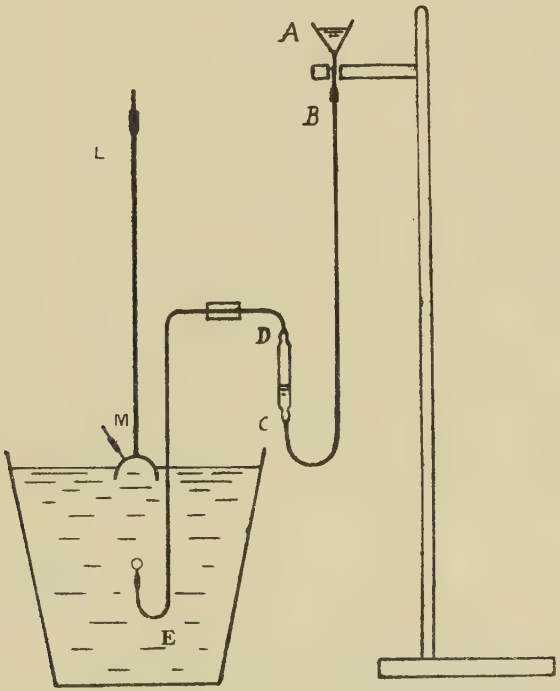
* 'The World of Sound,' p. 71 (London, 1921). Sir W. Bragg was kind enough to inform me that these researches of Sir R. Paget have never been published elsewhere.

† *Physica*, iii. p. 91 (1922).

‡ This was also remarked by A. Stromann, *Zeitschr. phys. chem. Unterr.* xxxvi. p. 251 (1923).

from filling the bend E. If that should happen the air-bubbles would still form, but the sounds would be much fainter and hardly to be heard except when applying the ear to the side of the pail; only if the bend E remains open is it possible to obtain a distinct sound for each bubble. The pitch is not always constant; it sometimes rises or falls or is subject to small irregular variations.

Fig. 1.



It is interesting that, after a series of rapidly escaping bubbles, the next ones, formed very slowly again, are always higher in pitch and their sound is more intense than at first.

We propose now to determine the pitch of a number of bubbles as a function of their volume, and this under different circumstances. Originally I always measured the total volume of a great number of bubbles; however, owing to the variations in pitch already mentioned, the

results were unsatisfactory. This difficulty was only overcome when the gas pipette of Professor Jordan came to my knowledge *. This beautiful and very simple instrument, so useful for physiological experiments, allows us to determine the volume of each individual air-bubble by catching it under a glass bell and introducing it into the capillary tube LM; the volume then is simply read as the length of the air-column. Before taking the reading on the scale the whole pipette is laid in an oblong trough filled with water, so that the volume is measured at a well-defined temperature, and can be reduced afterwards to the volume which the bubble had when it produced its sound in the pail. A preliminary control showed that the gases here used do not perceptibly dissolve during the time necessary for a measurement.

Simultaneous determinations of the pitch and the volume of each bubble can now be carried out. The pitch is determined by ear, taking for comparison the sound of a tuning-fork (C 264 VD about) and estimating fractions of half a tone. This determination is not very accurate, owing to the considerable difference between the two sounds, the short duration of the bubble sounds, their variations, and their small intensity. The mean error appears to be of the order of a fifth of a tone. Moreover the determination of the octave to which the sound belongs is very difficult for me, so that there remains an uncertitude of a factor 2 in the absolute values of the vibration numbers.

2. *A Theory for the Sounds of Air-Bubbles.*

The bubbles to which our measurements refer have diameters of 3 to 6 mm. Spherical resonators of that size would give sounds with a frequency of about 100,000 V.D., which is already beyond the limit of audibility. The observed frequencies are of the order of 2000. Another explanation is therefore needed.

We will suppose that the bubbles give a sound because they pulsate in closing. Periodically the bubble expands and contracts, the surrounding water being the inert mass which is set in vibration, while the elasticity is due to the air of the bubble.

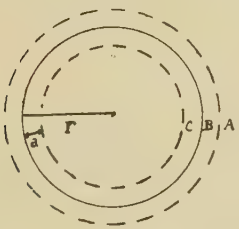
* Pflüger's *Archiv*, clxxxv. p. 311 (1920). I most cordially thank Prof. Jordan, who was so kind to lend me one of his pipettes.

A formula for the frequency of such pulsations may be derived in a quite elementary way. We will simply express that the potential energy accumulated during the compression till the moment when the volume is reduced to its minimum value (C, fig. 2) is equal to the kinetic energy of the water particles at the moment when half the expansion has taken place and the volume of the bubbles has again recovered its equilibrium value (B, fig. 2).

Let the radius r oscillate according to the law

$$r = r_0 + a \sin \frac{2\pi t}{T}.$$

Fig. 2.



At the moment when the radius of the bubble has decreased by a distance x the volume has decreased in the proportion $\left(\frac{r-x}{r}\right)^3$; if the compression is adiabatic in a gas for which $\frac{c_p}{c_v} = k$, the pressure will now be given by

$$\frac{p}{p_0} = \frac{{v_0}^k}{v^k} = \left(\frac{r}{r-x}\right)^{3k}.$$

The excess of the pressure inside over the pressure outside, being always a small fraction of the normal pressure, may be written

$$p - p_0 = \frac{3kpx}{r}.$$

Consequently the potential energy at minimum volume is

$$-\int_{V_0}^{V} (p-p_0)\,dV = \int_0^a \frac{3kpx}{r} \cdot 4\pi r^2\,dx = 6\pi kpra^2. \quad (1)$$

The kinetic energy is determined by the motion of the water, which for symmetry reasons is directed radially. The velocity of the wall of the bubble is

$$\frac{dr}{dt} = \frac{2\pi a}{T} \cos \frac{2\pi t}{T},$$

and that of a particle at a distance R

$$\frac{r^2}{R^2} \cdot \frac{2\pi a}{T} \cdot \cos \frac{2\pi t}{T}.$$

At the moment $t=0$ these velocities have their maximum value $\frac{r^2}{R^2} \cdot \frac{2\pi a}{T}$, and the total kinetic energy of all the volume elements of density ρ becomes

$$\frac{1}{2}\int \left(\frac{dr}{dt}\right)^2_{\max.} dm = \frac{\rho}{2}\int_r^\infty \frac{r^4}{R^4} \cdot \frac{4\pi^2 a^2}{T^2} \cdot 4\pi R^2 dR = \frac{8\pi^3 \rho r^3 a^2}{T^2}. \quad . \quad . \quad . \quad (2)$$

The integration is extended to the limit ∞, because we assume that the bubble is surrounded by a very great water volume. Putting the expressions (1) and (2) equal to each other gives the period and the frequency :

$$T^2 = \frac{4\pi^2 \rho r^2}{3kp}; \qquad N = \frac{1}{T} = \frac{1}{2\pi r}\sqrt{\frac{3kp}{\rho}}. \quad . \quad . \quad (3)$$

Let us compare this last expression (3) with that for the frequency of a spherical resonator with rigid walls * :

$$N = \frac{0{\cdot}715}{r}\sqrt{\frac{kp}{s}} = \frac{0{\cdot}715}{r}\sqrt{\frac{kp(1+\alpha t)}{s_0}},$$

where s is the density of the gas in the bubble, t the temperature in degrees C. We see how different the results are which correspond to the "rigid theory" of Sir R. Paget and to our "pulsation theory." According to our view the frequency is $2{\cdot}6\sqrt{\frac{s}{\rho}}$ times smaller—that means, about 80 times—so that the sound is transposed at once into the audible region. In our case it is chiefly the liquid that matters (in the other case it would be the gas) and the temperature is without influence. For both

* *Cf.* Rayleigh, 'Theory of Sound,' §§ 330 and 331.

theories the frequency is inversely proportional to the radius of the bubble.

We will see now if the properties of such pulsations correspond to the experimental data.

Experimental Results.

3. *Influence of the Volume of the Bubbles on the Pitch.*

With each of the terminal tubes two or three bubbles are formed, and their pitch and volume are determined. The current must be so slow that no more than one or two

Table I.

Volume and Pitch.

V.	N.	$\log N + \frac{1}{3} \log V$.
c.c.		
0·0211	1940	2·729
·0211	1880	·717
·0211	1960	·734
.0254	1805	·724
·0322	1710	·736
·0265	1805	·731
·0601	1370	·730
·0519	1540	·759
·0644	1350	·733
·0547	1410	·729
·1105	1150	·742
·0958	1210	·747
	Mean....	2·734±0·003 m.e.

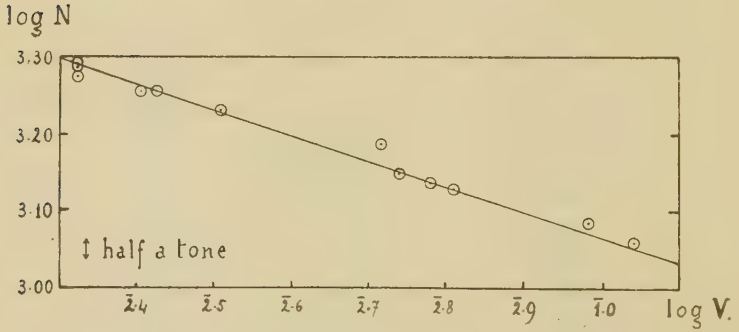
bubbles are developed in a minute, otherwise the results become less accurate (see § 4). In Table I. the frequencies and the volumes are given, and $\log N + \frac{1}{3} \log V$ is calculated, which, being practically constant, shows that N is inversely proportional to r. The same relation follows from fig. 3, where the slope of the straight line is 1 : 3·2, so that N is found inversely proportional to $r^{0·96}$; this is sufficiently close to the theoretical law, the deviations being half a tone for one single point only and for all the others smaller than a fifth of a tone, which is the mean error of a measurement.

The experiments only extend over one octave. Lower tones are difficult to obtain, because the bend E of the tube fills with water; it is equally difficult to obtain higher tones, for when the opening is chosen gradually narrower the pitch of the sound after reaching a maximum seems to fall again.

4. *Influence of the Velocity.*

When bubbles form with one determinate tube and increasing velocity the sound deepens more and more; the effect is especially marked for high tones. This influence of the velocity of outflow on the pitch is only indirect and due to its influence on the volume of the

Fig. 3.



air-bubbles. The relation between log N and log V is the same as in fig. 3, only the points are more scattered and the deviations doubtless exceed the limits of the experimental error; it is probable that currents in the water cause irregular deviations from the spherical form of the bubble.

5. *Influence of the Temperature.*

A series of measurements are now made with air-bubbles in water of different temperatures between 10° and 65°. Only two terminal tubes are used. When the temperature at which the bubble forms differs appreciably from that at which its volume is measured, it is necessary to take into account the change in the tension of the saturated water vapour w (in mm. of mercury). For two

different temperatures, T and T′, the partial tensions of the air are connected by the equation

$$\frac{760-w}{T}V=\frac{760-w'}{T}V',$$

from which V/V′ is derived.

The quotient k depends only very little on the temperature; if we take for air $c_p=0{\cdot}24$, $c_v=0{\cdot}17$, and estimate for water vapour $c_p=0{\cdot}35$, $c_v=0{\cdot}27$, we find $k=1{\cdot}40-0{\cdot}00016\,w$.

TABLE II.

Influence of Temperature.

Value of $\log N+\frac{1}{3}\log V$.

t.	Preliminary experiments.	1st tube.	2nd tube.
10° C.....	2·736	—	2·743
15	—	2·727	—
25	·710	—	·714
35	—	·739	·734
46	—	·732	—
49	·733	—	·714
56	—	·734	—
62	—	·735	—
65	·717	—	—

General mean.... 2·728±0·003 m.e.

If the sound is due to pulsations a change of temperature from 10° to 60° C. should give no appreciable change in pitch. On the contrary, if the bubble vibrates as a rigid resonator, the frequency depends on $\sqrt{\frac{k}{s}}$, where s is the density of the air saturated with water vapour, so that between 10° and 60° the pitch would rise over more than a full tone (see Table II.).

As Table II. shows, the observations prove unambiguously that the temperature has no influence, and therefore confirm the pulsation hypothesis. The results of the two terminal tubes are in good agreement with each other, although the sounds differ by a quint.

6. *Influence of the Density of the Liquid.*

It is evident that the experiments which we now describe will provide a decisive criterion between the two possible interpretations of the bubble sounds. In the rigid theory the surrounding liquid has no influence on the pitch of the cavity; but in the pulsation theory the frequency must be inversely proportional to the square root of the density of the liquid, and as this may be varied easily in the proportion 2 : 1, a good check is possible.

Table III.

Influence of the Liquid.

ρ.	V.	N.	$\log N + \frac{1}{3}\log V$.	$\log N + \frac{1}{3}\log V + \frac{1}{2}\log \rho$.
	c.c.			
0·82	0·0148	2440	2·778	2·735
0·82	·0254	1990	·768	·725
0·82	·0211	2110	·767	·724
1·00	·0222	1825	·711	·711
1·10	·0234	1775	·707	·727
1·10	·0256	1670	·675	·695
1·26	·0239	1670	·685	·735
1·50	·0325	1300	·611	·699
1·73	·0262	1320	·597	·716
1·96	·0177	1400	·565	·711
2·05	·0365	1180	·595	·751
2·05	·0428	1055	·568	·724
			Mean....	2·721 ± 0·003 m. e.

Successively bubbles were formed in alcohol, in water, and in a solution of mercurinitrate in diluted nitric acid; this last solution, when hot, could easily dissolve so much salt that the density amounted to 2. We know from the last paragraph that the temperature has no influence on the frequency of the sound. Wishing to avoid uncertain corrections, we surrounded the capillary tube of the pipette by a cylinder with water having the same temperature as that in which the bubbles were formed.

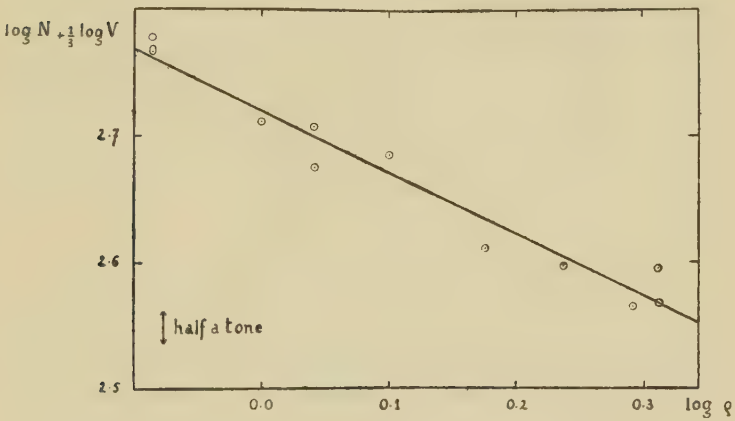
The results of our experiments are summarized in Table III. In column 4 the logarithm of the "reduced

frequency" (frequency for a bubble with volume 1) is found; it appears that the pitch falls systematically when the density is increased. In column 5, on the contrary, the numbers are constant, which proves that the frequency is really inversely proportional to $\sqrt{\rho}$; the same follows from fig. 4.

7. *Influence of the kind of Gas.*

After having varied the liquid we varied also the kind of the gas. Hydrogen and butane were investigated; both times, directly after the measurement, another series

Fig. 4.



of measurements was made with air under exactly the same experimental conditions. The hydrogen was made from Zn and H_2SO_4, the butane from ethyliodide and sodium amalgam, the gases being not purified. The whole apparatus was first filled with the gas, so that all air was expelled, and then bubbles were formed. The experimental results are summarized in the following short list:—

Hydrogen (7 measurements)	$\log N + \frac{1}{3}\log V = 2{\cdot}719 \pm 0{\cdot}003$
Air (11 measurements)	$2{\cdot}718 \pm 0{\cdot}003$
Butane (11 measurements).....	$2{\cdot}684 \pm 0{\cdot}003$
Air (9 measurements)	$2{\cdot}727 \pm 0{\cdot}003$

There cannot be doubt about the conclusion. Hydrogen gives the same result as air, which fact is entirely

consistent with the pulsation theory, because here it is only the value of k that matters, and this is the same for the two gases. With the rigid theory the frequencies should be in the proportion of the square roots of the densities, *i. e.*, in the proportion 2·7 : 1! On the contrary, there is a distinct difference between air and butane, due to the difference in the values of k. From the observed difference we deduce for butane $k=1{\cdot}15$. In this gas the exact value of the constant has not been determined yet by other methods, but from an extrapolation from methane, ethane, propane, about 1·11 would follow. The difference is not far beyond the limits of the experimental error, and may be attributed also to the presence of impurities in the gas.

It is not impossible that the determination of bubble sounds could be developed into a micromethod, allowing the measurement of $k = \frac{c_p}{c_v}$ for gas volumes of the order of 1 c.c. For the moment the value of k derived from a series of ten bubbles is still liable to be in error by nearly 2 per cent.

8. *Influence of the Form of the surrounding Water Mass.*

A last confirmation of the pulsation theory, although only a qualitative one, is found in the fact that the pitch rises when the bubble is formed at a small distance under the water-level, and that it falls when the bubble is formed quite near the wall of the pail or near an immersed glass plate. In the first case the resistance against displacement in part of the surrounding volume has decreased, in the second case it has increased. The difference in pitch can amount to one full tone in either sense, while the volume of the bubbles is not appreciably influenced. In forming bubbles quite near the surface it is of course impossible to use the Jordan pipette, but one can count the number of bubbles which are formed while the liquid ascends from C to D (*cf.* fig. 1).

9. *Absolute Pitch.*

As formula (3) proves to describe the bubble sounds accurately and in all details we can attempt to remove with its help the uncertainty concerning the exact octave.

Comparing the different series of observations on air- and hydrogen-bubbles, we derive the following values of $\log N+\frac{1}{3}\log V+\frac{1}{2}\log\rho$:—

1st series.....	2·734 (12 observations).
2nd series.....	2·728 (13 observations).
3rd series.....	2·721 (12 observations).
4th series.....	2·719 (7 observations).
5th series.....	2·718 (11 observations).
6th series.....	2·727 (9 observations).
Mean....	2·725

That the differences between the series exceed their probable error is probably to be attributed to the variations in the barometric height; this I unfortunately always assumed to be 760 mm., because I underrated the precision of my measurements.

The weighted mean of all the determinations gives the value 2·725 or $Nv^{\frac{1}{3}}\rho^{\frac{1}{2}}=531$, and

$$N=\frac{531}{r\sqrt{\rho}}\cdot\left(\frac{3}{4\pi}\right)^{\frac{1}{3}}=\frac{330}{r\sqrt{\rho}}.$$

We compare this with the theoretical formula (3), assuming the gas to be air or hydrogen and the pressure to be 760 mm.,

$$N=\frac{328}{r\sqrt{\rho}}.$$

The coincidence in the numerical factor is so close that an error of a factor 2 or $\frac{1}{2}$ is now practically excluded.

10. *Possibility of Capillary Vibrations.*

A third possible hypothesis would be that the bubbles execute capillary vibrations, because every deformation results in an increase of the surface area. However, the frequency of such vibrations has been calculated * and is equal to $N=1\cdot33/r^{\frac{3}{2}}$ (for the fundamental vibration of an air-bubble in water). This disagrees with the results in § 3, where we found $N\propto r$; moreover, if this hypothesis were right, changing the kind of liquid would not only influence the pitch by the varying density, but also by the changed capillary constant. Finally, it is obvious

* *Cf.* Lamb, 'Hydrodynamics.'

that the frequency of capillary vibrations of our bubbles would be only about 15, and thus in complete contradiction with the experimental results.

For these reasons the hypothesis of the capillary vibrations seems definitely excluded.

Conclusion.

From our experiments it follows that the bubbles formed when air escapes from an orifice under water give their sounds by pulsation in the way described in our introduction; the frequency is quantitatively determined by equation (3). The possibility that these sounds could be interpreted as vibrations of a resonator with rigid walls seems excluded. A third possibility, that of capillary vibrations, would be also inconsistent with our experiments.

It remains to investigate if larger bubbles give additional vibrations of other kinds and if the sounds of falling drops cannot have the same origin as the bubble sounds.

XVII. *Thermodynamic Principle governing Stationary States.* *By* B. Bružs, *Ph.D.**

1. *Stationary States.*

LET two infinitely large reservoirs, differing between themselves in the intensity factor (potential) of one of the energy forms they contain, be connected by a "bridge," *i. e.*, an energy-conducting system, with the aid of which the potential difference of the reservoirs is being equalized. Under the stress of the applied potential the bridge will in general undergo certain changes and assume properties which it did not have before the contact was established with the reservoirs. After a certain (usually long) interval of time the bridge approaches a state commonly called stationary. This final state is characterized by the fact that all properties of the bridge, including the energy content, become independent of time.

* Communicated by J. H. Wolfenden, M.A.

A stationary state should be distinguished from a thermodynamic equilibrium, to which it bears a superficial resemblance, as regards the independence of time and the way it is attained. One has to remember that a stationary system not only owes its time-independent properties to an externally applied constant potential difference, but also exists at the expense of the latter, and, further, that these properties change when the potential difference is withdrawn.

The form of the bridge in the stationary systems we are going to consider plays a subordinate rôle, and for the sake of simplicity we will assume it to be a cylinder with the inner volume conducting the energy. We will have to distinguish the rôle of three different surfaces. Through one of the end-walls energy will be taken up by the bridge and through the other end-wall will be given out. For an unambiguous definition of the system the properties of the side-walls will also have to be known. The side-walls may be insulators, or else energy may be exchanged with the surroundings through them. Considering the conservation of energy expressed by the first law, which is not restricted to any particular system, we obtain for a stationary system the result that the balance of the energy exchanges through the three different walls has to be zero. This is the first restriction governing stationary systems.

The successful interpretation of stationary states will also depend on the correct application of the law of conservation of matter. The equalization of the potential difference between the reservoirs will obviously be connected with a flux of *energy* from the reservoir with the higher potential to that of the lower one. This flux, on the other hand, will be generally inseparable from a migration of matter, since all the energy forms we are going to consider more closely are connected with matter. Two cases will have to be distinguished. In one case the energy-transporting matter will move only in one direction through the bridge. It is obvious that in this case the reservoirs will have to consist of this sort of matter (*e. g.*, stationary sublimation) or else be penetrable to it (electronic conductors). In the second case the energy transporting material of the bridge moves backwards and forwards between the walls and there is no one-sided transport of matter (gaseous heat

conduction). The first case can be analyzed much more easily than the second on account of the evidence of the transported matter we have in many cases (*e. g.*, Faraday's Law). Stationary electrolysis should really be considered an intermediate case. The ions, reactive at the electrodes, are transported one-sidedly, the rest of the ions complete a cycle ; in one part of the cycle they are transported electrically, in the other by diffusion. The fact that the bridge moves in space in the first case and that in the second case no additional laws are known to help the interpretation of the phenomena do not, however, interfere, as will be shown later, with a general thermodynamic treatment of all these stationary states, though it will be very important to recognize the particular way in which the energy carriers act.

In instances of electric conduction in the bridge we have a definite knowledge of the exchange of energy through the side-walls (Joule's Law); the same is true for cases with insulating walls (energy exchange zero). It is clear that a complete balance, and consequently a solution of stationary states, would be possible in most instances if we found a law governing the amount of energy that enters and leaves the system.

From the preceding it will also be clear that the energy transported by the bridge is connected with the migration of the energy-carrying matter. Since the latter, however, undergoes friction, or, more generally speaking, irreversible changes, the second law of thermodynamics will be inapplicable unless additional assumptions are made [6]. F. Kohlrausch [1] was one of the first to stress this inapplicability of the second law. He also proposed a theory to the effect that an electrical (material !) current is always connected with a thermal one, and *vice versâ*, in agreement with the arguments used in this paragraph. A quantitative solution of the problem was impossible, however, since the proportionality factor connecting the two currents remained unknown.

E. D. Eastman[2a], the author of the most modern theory in this field, gave a formal solution for nonisothermal stationary systems on very much the same grounds as F. Kohlrausch, arbitrarily defining a certain " heat of transfer " (Q*) accompanying the movement of matter. We think that Eastman's theory gives the correct form of the equations for stationary states only in cases where

one-sided material transport takes place. The cyclic character of the material movement in cases like the Soret phenomenon has, it seems to us, been neglected by this theory.

It is characteristic for both theories that they leave for stationary systems one unknown to be independently determined.

Certain theories of a still more narrow range of applicability are usually based on the construction of *approximately* valid reversible cycles with a subsequent application of the second law (Thomson's theory of thermoelectric phenomena), or on *special* mechanical *models* (Kinetic theory of the Feddersen-Knudsen effect [7]).

2. *Irreversibility in Stationary Systems.*

We have mentioned already that a fundamental distinction has to be made between stationary states and thermodynamic equilibria on account of a constant annihilation of potential difference in stationary states, with a resulting inapplicability of the second law of thermodynamics. When this circumstance is neglected stationary states may be easily mistaken for thermodynamic equilibria, and *vice versâ*.

For instance, a gas in a gravitational field very much resembles a stationary system, particularly as regards the gradual change of properties so characteristic of stationary states. The real resemblance to stationary states, however, lies only in the fact that, due to an external stress which has here the form of a field of force, the gas has acquired an extra parameter (degree of freedom) as compared to usual thermodynamic equilibria. The problem can still be solved by application of the second law, because no annihilation of potential difference is taking place. The same absence of annihilation of potential difference permits the thermodynamic treatment of the osmotic equilibrium, where a concentration difference is balanced by a pressure difference.

Lability of a system may also be the cause of confusion. $BaSO_4$ may, as is well known, have different solubilities at constant temperature depending on the grain size. These systems of different grain size resemble stationary systems in so far as the disappearance of the extra parameter (surface energy) causes the systems to go over

into the most stable state. They belong, however, to equilibrium systems on account of the assumed and usually attained absence of annihilation of surface energy during the solubility measurement. When this assumption is not fulfilled (solution with $BaSO_4$ of different grain sizes) we *may* have a stationary state, *e. g.*, in certain cases when only two different grain sizes are present.

Out of the large number of possible stationary states to which belong oscillators, systems with periodic fluctuations in the externally applied potential, radioactive "equilibria," chemical and photochemical stationary states, we will choose for further consideration only systems of the "bridge" type described in the preceding paragraph. Some of the most important properties of these "bridges" will now be discussed.

The changes that take place in the "bridge" on application of the external potential consist in the effect of the appearance of a new kind of potential along the axis of the bridge, *e. g.*, on application of an E.M.F. to the Zn end-walls of a $ZnSO_4$ solution a concentration gradient of $ZnSO_4$ appears in the bridge. We selected this example to show, first, that the "induced" potential has, as is well known, the properties of an opposed force (polarization). It can further be seen clearly from our example that the magnitude of the effect is such that when a corresponding concentration gradient is applied to Zn electrodes the original E.M.F. will result. This explains the important fact that a reciprocity exists between the inducing (ψ') and induced (ψ'') potentials, with a corresponding existence of inverse effects for every "direct" effect. This reciprocity is of a quite general nature for all our stationary systems, but it must be emphatically stated that it has nothing to do with a reversibility of the processes that are causing these effects. On the contrary, the irreversibility of the processes can be clearly recognized from the fact that a "Joule heat" is constantly being dissipated through the side-walls of the systems, with non-isolating walls to keep them at constant temperature, and particularly from the fact that $\bar{F}$ falls off along the axis of the cylinder.

In analogy to "cycles" in systems where the processes take place reversibly one can construct and study to advantage complicated stationary systems by the aid of "circulation machines" described in an earlier paper [9].

For the further theoretical treatment of stationary states we will have to keep in mind the important circumstance pointed out in this paragraph that *the processes* which cause the giving off or taking up of energy at the end-walls of the bridge *will be functions of two variable parameters* at least, viz., the inducing and the one or more induced potentials

$$(dG = \frac{\partial G}{\partial \psi'} d\psi' + \frac{\partial G}{\partial \psi''} d\psi'' + \ldots,$$

where G is an arbitrary thermodynamic quantity).

3. *General Principle governing Stationary States.*

The description of stationary states given in the preceding paragraphs permits us to present the problem of the present paper in quite a general way. From the purely phenomenological standpoint we know that application of potentials to "bridges" causes quite definite and experimentally measurable stationary effects. We will mention the most important ones: a temperature difference (dT) for instance may cause three different effects—an E.M.F. (dE) in an electric conductor (Seebeck effect), a pressure difference (dP) in a porous plug (Fedder-sen-Knudsen effect), or a concentration gradient (dc) in a solution (Ludwig-Soret effect). There are three effects (Peltier, Dufour-Knudsen, and one experimentally hardly investigated effect [9] which represent the inversion of the ones just mentioned. A reciprocal pair of effects is known for electrical potential gradients and concentration gradients ("Hittorf"-polarization and "Helmoltz-" concentration-cell effects). The osmotic effects connect pressure and concentration gradients. The knowledge of E.M.F.-pressure and concentration-concentration [2 c] effects is yet very scant. For any of these effects the experimentally determinable *coefficients* take the form of a ratio of two potentials, *e. g.*, $d \ln N/dT$ will be the Soret coefficient. This existence itself of definite coefficients shows that the problem of stationary states must have a definite solution, and the question arises whether the experimentally determined values represent (complicated) functions of the dynamic properties of the systems, or else may find a comparatively simple expression in terms of the usual thermodynamic properties of the

system, *i. e.*, properties that are determined in equilibrium systems or by the aid of the first law.

A formal justification for the last supposition may be derived from the fact, already mentioned, that stationary systems from the standpoint of Gibbs' phase rule are systems with an extra degree of variance represented by the applied potential. This fact, combined with the experimental evidence that stationary systems have a definite solution, permits the possibility that a *thermodynamic* restriction of an entirely general form may be governing stationary states in the way for instance that the dynamic factors disappear in the final equations by division [5] on account of a certain dualism of the processes which manifests itself in the existence of the two potentials.

The exposition of the matter in the first paragraph shows that stationary systems, which, as we will mention again, remain indefinite systems [6] from the standpoint of the second law of thermodynamics, receive a definite solution when one arbitrary restrictive assumption is made in form of a statement regulating energy changes at the end-walls. At this stage we introduce our special theory by postulating that the *boundary conditions* for the processes at the end-walls of the bridge are such that no change occurs in the free energy (F, Gibbs' ζ) of the moving component, or that the change in the total energy content ($\bar{H}$) corresponding to the wall reaction can be expressed as the change in entropy ($\bar{S}$) for the same reaction multiplied by the absolute temperature (T) at the wall.

It is necessary to point out at once that this assumption should in no way be confused with a statement that the second law is applicable to stationary states. The extra parameter that stationary systems possess has vectorial properties, and the restricting condition of our postulate concerns the variation of properties in the infinitesimally narrow boundary region where the energy exchanges with the surroundings take place. When a mole of material is transported along the axis of the cylinder the property *change* will be $\frac{dG}{dx} . dx$. Considering the narrow boundary region with dx approaching zero we will have to distinguish the cases where the property

gradients (dG/dx) are finite or infinite. In the first case the property change will be zero; in the second case, however, it will be finite.

Let us investigate more closely the end-wall. Here three cases are worth mentioning. If we had assumed the second law to be valid the free energy should be represented by a horizontal line. This, however, would only be possible if the bridge had no connexion with the process of equalization of potential. Out of the remaining possibilities we have chosen the one that *the free energy of the component on passing through the boundary changes continuously*, and not in the way of the entropy, which changes discontinuously and represents the second possibility mentioned above. Since $\bar{S}$, in contrast to $\bar{F}$, changes discontinuously, we have the case never occurring in thermodynamic equilibria that $\triangle H$ (considered for $dx \rightarrow 0$) may be finite and equal to $T\triangle\bar{S}$ as we assume it in our postulate, without F being constant in the whole system.

The thermodynamic restriction which we have postulated to govern stationary states can obviously not be derived from the second law of thermodynamics. It is just as independent from it as is the statement of the third law $S_0=0$. The equilibrium condition $\bar{F}=$const. required by the second law assumes for *stationary systems* the form that $\partial F/\partial x$ has always a *finite* value or is equal to zero. The resulting relation $\triangle H=T\triangle S$ for the wall process confusingly resembles, to be sure, the relation of the second law, though both result from different causes.

The application of the new principle to stationary systems is very simple when the wall process is unambiguously known, as, *e. g.*, in all cases with one-sided material transport. A certain difficulty presents itself in systems without one-sided material transport. Here, however, a consideration [9] of the possible modes of the participation of the material in the equalization of the applied potential leads to the conclusion that the energy carriers move in one direction under the applied potential (ψ'), and return under the induced potential (ψ''). By comparison with the easily interpretable case of a "Reststrom" it follows that in these cases $\triangle G$ of the wall

process must become proportional to $\partial G/\partial\psi''$. Applying our principle, we then obtain

$$\triangle\bar{H}=\text{const}\,.\,\frac{\partial\bar{H}}{\partial\psi''}=\text{const}.\frac{\partial T\bar{S}}{\partial\psi''}.\quad .\quad .\quad .\quad (1)$$

The rest of the calculation is the same in both cases: one puts up a balance according to the first law and solves for $d\psi''/d\psi'$ the coefficient of the effect.

4. *General Mathematical Solution for Stationary Systems of the "Bridge" Type.*

In our discussion we will assume that all the energy exchange between the reservoirs is due only to the one-sided or circulatory migration of the energy carriers. If actually some energy is transported through the bridge independently of this material migration, *e. g.*, by radiation, we assume that this energy is in no causal connexion with the processes we are considering, and is in no way affecting the energy balance.

The simplest case of stationary states that can be solved with the aid of our principle is a bridge with one-sided material transport and insulating walls (Case A). Our principle gives for the wall process $d\triangle H=dT\triangle S$, where $\triangle H=H_B$ (in the bridge)$-\bar{H}_R$ (in the reservoir). We further have the condition of an insulating wall

$$d\bar{H}_B=0.\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad (2\,a)$$

Both conditions combined give

$$d\bar{F}_R+dT\bar{S}_B=0,\quad .\quad .\quad .\quad .\quad .\quad .\quad (2\,b)$$

or

$$\frac{\partial\bar{F}_R}{\partial\psi'}d\psi'+\frac{\partial T\bar{S}_B}{\partial\psi'}d\psi'+\frac{\partial T\bar{S}_B}{\partial\psi''}d\psi''=0.\quad .\quad .\quad (2\,c)$$

When the side-walls of the bridge are in direct contact with the surroundings we will assume that Joule's Law holds in all cases, *i. e.*, that the loss through the side-walls during the migration along the axis of the cylinder is equal to the loss in free energy of the energy carrier (dF_B). This assumption is in complete harmony with our postulate: the migrating matter assumes the same potential gradient that is existing in the surroundings,

so as not to create a discontinuous change in free energy. Consequently we have for the second case (Case B)

$$d\bar{H} = d\bar{F}_B, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3\,a)$$

or

$$d\bar{T}S_B = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3\,b)$$

or

$$\frac{\partial \bar{T}S_B}{\partial \psi'} d\psi' + \frac{\partial \bar{T}S_B}{\partial \psi''} d\psi'' = 0. \quad . \quad . \quad . \quad (3\,c)$$

Two more cases can be derived from the preceding equations when circulatory migration is considered (Cases A′ and B′). The analysis of the circulation mechanism mentioned in the preceding paragraph shows that the condition for these states are

Case A′: $d\dfrac{\partial \bar{H}_B}{\partial \psi''} = 0,$

or

$$\frac{\partial}{\partial \psi'} \frac{\partial H_B}{\partial \bar{\psi}''} d\psi' + \frac{\partial}{\partial \psi''} \frac{\partial \bar{H}_B}{\partial \psi''} d\psi'' = 0. \quad . \quad (4\,c)$$

Case B′: $d\dfrac{\partial \bar{T}S_B}{\partial \psi''} = 0,$

or

$$\frac{\partial}{\partial \psi'} \cdot \frac{\partial TS_B}{\partial \psi''} d\psi' + \frac{\partial}{\partial \bar{\psi}''} \cdot \frac{\partial \bar{T}S_B}{\partial \psi''} d\psi'' = 0. \quad . \quad (5\,c)$$

We can summarize the results by stating that in stationary systems, depending on the property of the side-wall, one thermodynamic property of the energy transporting matter assumes a constant value; it is $\bar{H}$ rsp. $\partial H/\partial \psi''$ in systems with insulating walls, and $\bar{T}S$ rsp. $\partial TS/\partial \psi''$ in systems having thermal contact with the surroundings.

5. *The most important Cases solved with the Aid of the Principle.*

(*a*) Suppose the reservoirs and the bridge, all containing a binary solution with the mole fraction N_2 of the solute, be divided from each other by rigid membranes permeable to solute only and a pressure increment dP imposed on one of the reservoirs. It is easy to see that a concentration gradient will automatically appear in the bridge following the migration of the solute from one reservoir to the other. Applying equation 3 *c* to our

case we obtain, introducing $\bar{V}$ the partial molar volume and V the volume of a mole of the solution,

$$T\frac{\partial \bar{S}_2}{\partial \ln \bar{N}_2} d\ln N_2 + T\frac{\partial \bar{S}_2}{\partial P} dP = 0, \quad . \quad . \quad . \quad (6)$$

and

$$\frac{d\ln N_2}{dP} = -\frac{\frac{\partial \bar{H}_2}{\partial P} - \bar{V}_2}{T\frac{\partial \bar{S}_2}{\partial \ln \bar{N}_2}} = \left[-\frac{V_2}{RT}\right]_{N_2 \to 0} . \quad . \quad (6\,a)$$

When we consider that out of the total pressure excess (dP) on one of the reservoirs only the fraction $N_2\bar{V}_2/V$ is directly affecting component 2, equation (6 *a*) may be transformed for the solute into

$$d\sqcap_2 = \frac{N_2 V_2}{V} dP_2 = -\frac{N_2 \bar{V}_2}{V} \times \frac{T\frac{\partial S_2}{\partial \ln N_2}}{\frac{\partial H_2}{\partial P} - V_2} d\ln N_2 = \left[-RT dc\right]_{N_2 \to 0} . \quad . \quad (6\,b)$$

Here $d\sqcap_2$, the specific pressure lying on component 2 of the solution, *i. e.*, on the solute, obviously represents van't Hoff's dynamic concept of the osmotic pressure which has been used by Nernst [3] and Planck [4] for the solution of the problems of diffusion and concentration polarization in dilute solutions (expression in brackets). Our equation leads to a diffusion law which, contrary to Fick's Law, claims validity for any concentration, and which is reciprocally valid for *both* components of the solution [11]. This generalized Berthelot-Fick equation has the form y_N = diffusing mols of i per sec. cm.^{2} =

$$w_i \frac{N_i}{V} T \frac{\partial S_i}{\partial \ln N_i} \cdot \frac{d\ln N_i}{dx} = \left[-wRT\frac{dc}{dx} = -d\frac{dc}{dx}\right]_{N_2 \to 0} . \quad (6\,c)$$

Here w_i is the mobility of the component in cm. mol/sec. dyne, and $w \,.\, RT = d$ the diffusion coefficient (Nernst). The factor $\frac{1}{V_i}\frac{\partial TS_i}{\partial P}$ reduces $d\sqcap_i$ to a mechanical pressure, and consequently disappears in (6 *c*), where only the driving mechanical pressure must be considered (*cf.*

equation (11). (*b*) The E.M.F. of a concentration gradient is the second problem that can be solved with the aid of our principle. When the reservoirs are first-class electrodes and the bridge a solution containing the ion active at the electrode then the application of an E.M.F. causes the appearance of a concentration gradient in the bridge (concentration polarization). Applying to this system equation (3 *c*) we obtain

$$T\frac{\partial \bar{S}_+}{\partial \ln N_2} d\ln N_2 + T\frac{\partial \bar{S}_+}{\partial E} dE = 0, \quad . \quad . \quad . \quad (7)$$

and *

$$\frac{d\ln N_2}{dE} = -\frac{z_+ f}{T\dfrac{\partial \bar{S}_+}{\partial \ln N_2}} = \left[\frac{zf}{RT}\right]_{\text{ideal}} . \quad . \quad . \quad (7\,a)$$

Here f represents the Faraday constant and z the valency of the ion. The idealized equation for dilute solutions (in brackets) gives the value of the corresponding cell without liquid junction, showing that an equation $\partial \bar{S}_+/\partial \ln N_2 = -R$ is equivalent to the assumption that liquid potentials disappear on very high dilutions ($u=v$). Equation (7 *a*) agrees in the limits of the comparatively large experimental error with actually determined concentration coefficients of ionic entropies [8]. Transport equations of the Nernst-Planck type derivable from (6 *c*) are in perfect agreement with (7 *a*), which fact strengthens the correctness of the assumption lying at the base of both equations. They further agree for dilute solutions with the results of Nernst-Planck. The unsolved question of anodic slime is easily interpreted with the aid of our theory [10].

(*c*) Thermoelectric phenomena represent the next problem satisfactorily explained on the assumptions of our theory. The constancy of TS_e in the conductor, which is in thermal equilibrium with the temperature gradient of the surroundings (Case B), gives

$$(\bar{S}_e + C_e)dT - f dE = 0. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

* We prefer to put

$$T\frac{\partial \bar{S}_+}{\partial E} = z_+ f$$

in complete analogy to

$$T\frac{\partial S}{\partial P} = -\frac{\partial F}{\partial P} + \frac{\partial H}{\partial P}.$$

The alternative assumption, however, also leads to (7 *a*) [10].

Here and further on $\bar{C}$ is the partial molar specific heat at constant pressure. Remembering the derivation of (3 *c*), from which (8) is obtained, we find that the losses through the side-wall are equal to

$$d\bar{F}_e = d\bar{H}_e = -\bar{S}_e dT + f dE = \bar{C}_e dT. \quad . \quad . \quad . \quad (9)$$

Here $f dE$ is obviously the Joule and $-\bar{S}_e dT$ the Thomson heat, $\bar{C}_e dT$ being the effective heat-loss to the surroundings. Experimentally one can only measure the difference of the two E.M.F.'s of the two conductors. We consequently obtain for the Seebeck effect

$$\epsilon = \frac{dE_1 - dE_2}{dT} = \frac{\triangle\bar{S}_e + \triangle\bar{C}_e}{f} = \frac{T\triangle\bar{S}_e + T\triangle\bar{C}_e}{fT} \quad . \quad . \quad (8\,a)$$

Here $T\triangle\bar{S}_e$ represents, according to our fundamental assumption, the heat taken up from the surroundings at the wall or the Peltier heat (πf), and $T\triangle\bar{C}_e$ the *difference* in the effective heat exchanges of the two conductors with the surroundings. Since the latter ones compared to the Peltier heats are very small in all known cases, we obtain as close approximation the equation of Thomson (Lord Kelvin):

$$\epsilon = \frac{\pi}{T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8\,b)$$

For the change of the Seebeck coefficient with temperature we obtain

$$\frac{d\epsilon}{dT} = \frac{1}{f}\left(\frac{\triangle\bar{C}_e}{T} + \frac{\partial\triangle\bar{C}_e}{\partial T}\right), \quad . \quad . \quad . \quad (8\,c)$$

in agreement with Thomson's second equation, when the same approximation is considered.

A particularly important result of our treatment of thermoelectric phenomena is the interpretation of the Peltier heat as $T\triangle S$ of the electrode process. This interpretation, contrary to Eastman's theory [2d], permits the experimental determination of absolute ionic entropies directly from measurements of Peltier heats.

(*d*) The most interesting result of our theory represents the solution of the Ludwig-Soret problem, which, though repeatedly attacked, had never yielded to the attempt to predict Soret coefficients from usual thermodynamic

data. (5 *c*) applied to this problem takes for the Soret coefficient the form

$$\sigma = \frac{d \ln N}{dT} = -\frac{1}{NT} \cdot \frac{\frac{\partial(\bar{C}_p + \bar{S})}{\partial N}}{\frac{\partial^2 \bar{S}}{\partial N^2}}$$

$$= \left[-\frac{1}{RT} \frac{\partial(\bar{C}_p + \bar{S})}{\partial \ln N} \right]_{N \to 0}, \quad . \quad (10)$$

a formula which gives the correct order of magnitude and the correct variation with the type of solute for the not very exactly known coefficient [9].

(*e*) As a last result attained with the aid of our theory we will only mention the problem of heat conduction where all four cases of section 4 can be distinguished, and where particularly the thermodynamic interpretation of the Feddersen-Knudsen effect is of interest [13].

6. *Transport Equations.*

It is very probable that the thermodynamic principle governing stationary states will find a more suitable formulation than the one given in this paper. The sole realization of the fact, however, that stationary systems probably are governed by a thermodynamic principle would mean a definite advance compared to the theory of Eastman, which apparently [2 *b*] postulates the dependence of stationary states on purely dynamic quantities which are indeterminable from common thermodynamic magnitudes.

On the other hand, we think that the fundamental properties of the apparently existing new principle have been correctly recognized in our postulate and in our equations.

Evidence of a general type for the validity of our theory is obtained from an investigation of the irreversible transport phenomena. We observed during the investigation of stationary systems that a postulate to the effect that " the force acting on a mole of a mobile substance in a potential gradient is proportional to the gradient of the ' latent heat ' $T\bar{S}$ of this substance " is in good agreement with our general knowledge of the phenomena. Applying this postulate, having a purely thermodynamic

form, we obtain for the mols of the energy carrier transported per unit section and unit time in the corresponding fields (subscript of y) the following equations :—

$$y_{\mathrm{P}} = \frac{w}{\mathrm{V}} \mathrm{T} \frac{\partial \mathrm{S}}{\partial \mathrm{P}} \frac{d\mathrm{P}}{dx} = \left[-w \frac{d\mathrm{P}}{dx} \right]_{\text{ideal}} \quad . \quad . \quad . \quad (11)$$

$$y_{\mathrm{N}} = \frac{w}{\mathrm{V}} \mathrm{T} \frac{\partial \bar{\mathrm{S}}}{\partial \ln \bar{\mathrm{N}}} \cdot \frac{d\mathrm{N}}{dx} = \left[-d \frac{dc}{dx} \right]_{\mathrm{N} \to 0} \quad . \quad . \quad . \quad (12)$$

$$y_{\mathrm{E}} = -\frac{u}{\phi} \mathrm{T} \frac{\partial \bar{\mathrm{S}}_+}{\partial \mathrm{E}} \frac{d\mathrm{E}}{dx} = -\frac{t_+}{\rho f} \frac{d\mathrm{E}}{dx} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$y_{\mathrm{T}} = \frac{w}{\bar{\mathrm{V}}} (\mathrm{S}+\mathrm{C}) \frac{d\mathrm{T}}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The first of these equations complies with the requirements of mechanics and corrects the simple mechanic equation (in brackets) for the Joule-Thomson heat

$$\left(\mathrm{T} \frac{\partial \mathrm{S}}{\partial \mathrm{P}} = -\frac{\partial \mathrm{F}}{\partial \mathrm{P}} + \frac{\partial \mathrm{H}}{\partial \mathrm{P}} \cong -\mathrm{V} \right).$$

The second equation is the generalized Berthelot-Fick equation, and the third one the common conductivity equation according to Hittorf (ϕ is the dilution of the conductor).—N.B. $uf\mathrm{T} \frac{\partial \bar{\mathrm{S}}_+}{\partial \mathrm{E}} = uz_+ f^2 = \lambda_+$.

The fourth equation is new, but apparently correct, since it explains, quantitatively at least, the phenomena investigated by Knudsen. $\frac{\mathrm{S}+\mathrm{C}}{\bar{\mathrm{V}}} \, d\mathrm{T} = \left[\frac{1}{\bar{\mathrm{V}}} \frac{\partial \mathrm{TS}}{\partial \mathrm{T}} \, d\mathrm{T} \right]$ represents the thermomolecular pressure, an analogue of the osmotic pressure.

These equations, which really go further than the solution of stationary states, are in complete agreement with our formulæ of stationary systems. This agreement is made evident when two transport equations are put equal to each other (conditions of statistical immobility in the bridge). The corresponding equations for stationary systems with non-isolating sidewalls and one-sided material transport result. The dynamic factor w of the transport equations disappears by division, thus clearly showing why stationary states are independent of the dynamic properties of the bridge.

The considerations of this section seem to us a particularly important indication in favour of our prediction of a new principle of a thermodynamic nature.

References.

(1) F. Kohlrausch, Pogg. *Ann.* clvi. p. 601 (1875); Wied. *Ann.* xxiii. p. 477 (1884), lxvii. p. 630 (1899).
(2 *a*) E. D. Eastman, J. Am. Chem. Soc. xlviii. p. 1482 (1926), xlix. p. 792 (1927), l. pp. 283, 292 (1928).
(2 *b*) C. Wagner, *Ann. d. Phys.* (5) iii. p. 629 (1929), vi. p. 370 (1930).
(2 *c*) G. S. Hartley, Trans. Faraday Soc. xxvii. pp. 1, 11 (1931); Phil. Mag. (7) xii. p. 473 (1931).
(2 *d*) E. Lange, *Th. Hesse Z. Elektrochem.* xxxviii. p. 428 (1932).
(3) W. Nernst, *Zeit. phys. Chem.* ii. p. 613 (1888).
(4) M. Planck, Wied. *Ann.* xxxix. p. 161 (1890).
(5) H. A. Lorentz, 'Les théories statistiques en thermodynamique,' §45. Teubner: Leipzig (1916).
(6) L. Onsager, Phys. Rev. xxxvii. p. 405 (1931), xxxviii. p. 2265 (1931).
(7) S. Weber, *Zeit. f. Phys.* xxiv. p. 267 (1924).

[The ideas of the present paper were gradually developed in the communications quoted below. They contain full particulars on many of the points just mentioned in section 5. On the other hand several mistakes, particularly in the derivations of the fundamental formulæ, have occurred there, due to uncertainty of the general principle at that time (heat losses through the side-walls). These mistakes are corrected, without particular reference, in the present communication representing the first broader analysis of the new postulate.]

8) "Peltier." *Zeit. phys. Chem.* A. cxlv. p. 470 (1929), A. clv. p. 392 (1931).
(9) "Soret." *Ibid.* A. clvii. p. 422 (1931).
(10) "Concentration Polarization." *Ibid.* A. clxi. p. 83 (1932).
(11) "Diffusion." *Ibid.* clxii. p. 31 (1932).
(12) "Thermoelectricity." *Z. Elektrochem.* xxxviii. p. 777 (1932).
(13) "Heat Conduction." (In preparation.)

Chemical Laboratories,
University of Latvia,
Riga (Latvia).

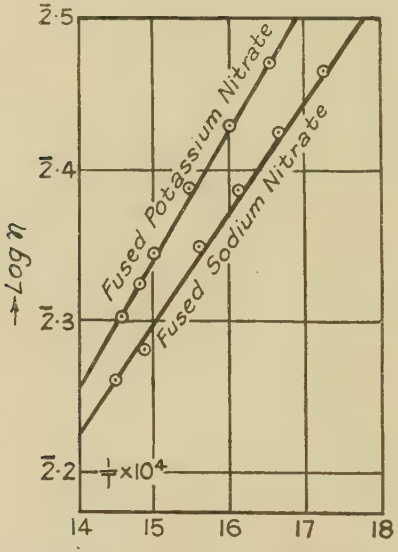
XVIII. *Viscosity of Fused Salts and Andrade-Sheppard Formula for the Viscosity of Liquids.* *By* Balbhadra Prasad *.

OF the various formulæ suggested connecting temperature and viscosity the Andrade-Sheppard formula $\log \eta = \alpha + \frac{\beta}{T}$ ('Nature,' March 1, March 29, and April 12, 1930) gives the most satisfactory result in the case of unassociated liquids. For the associated liquids Andrade proposes the formula $\eta = Ae^{\frac{b}{T-\theta}}$, which can be written as

* Communicated by the Author.

$\log \eta = \alpha + \frac{\beta}{T-\theta}$ ('Nature,' April 12, 1930). In these formulæ η denotes viscosity, α and β constants for the liquid concerned, and T the absolute temperature, θ a constant for the particular liquid used. A theoretical explanation of the formula for the unassociated liquids has been suggested by Andrade ('Nature' Nov. 14, 1931). The assumptions made in deducing the formula are not above criticism.

Fig. 1.

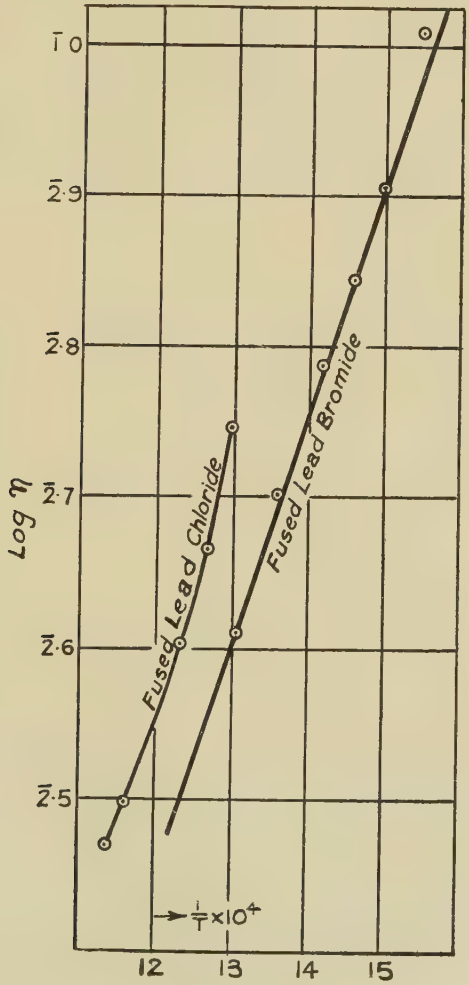


The object of the present investigation is twofold: first to see whether either of the two formulæ holds good for the fused salts or not; if it does, to see whether the fused salts behave like associated or like unassociated liquids. In figures 1–3 $\log \eta$ is plotted against 1/T.

As is evident from figs. 1 & 2, $\log \eta$ plotted against 1/T gives a straight line in the case of sodium nitrate, potassium nitrate, and lead bromide. The points do not lie on a straight line in as nice a manner as they do in the case of organic liquids; but then it has to be borne in mind that the measurements of the viscosity of fused salts are bound to be more inaccurate than those of the organic liquids, on account of the difficulty

encountered in maintaining the high temperatures used, constant and some other factors coming in on account of high temperatures.

Fig. 2.

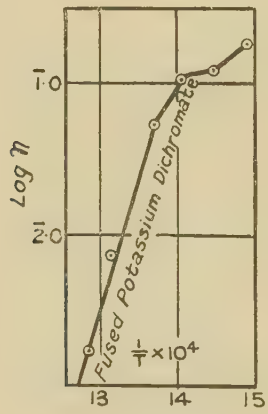


In the case of lead chloride $\log \eta$ plotted against $1/T$ does not give a straight but a slightly curved line. This is evidently due to the incomplete dissociation of lead

chloride into lead and chloride ions at low temperatures and the increase of dissociation with the rise of temperature. The lead chloride curve resembles water-curve, both water and lead chloride being associated at low temperatures, though the two associations are of different kinds. Like water, the viscosity of lead chloride is represented accurately by the formula $\log \eta = \alpha + \frac{\beta}{T-\theta}$.

In the case of lead bromide, $\log \eta$ corresponding to the lowest temperature alone, does not lie on the straight line on which the other points almost lie. Whether it is an experimental error or it is due to incomplete

Fig. 3.



dissociation of lead bromide at low temperatures cannot be said.

It is significant that though nitrates seem to be associated in solutions they seem to be completely dissociated in the fused state, otherwise a straight line would not have been obtained in their case.

The line obtained in the case of potassium chromate deviates too much from a straight line. The deviation is too much to be accounted for by electrolytic dissociation. The fused potassium dichromate on being heated above its melting-point perhaps dissociates into potassium chromate and chromium trioxide, which remains dissolved in the fused potassium chromate. It would be interesting to investigate by other methods whether

at temperatures used, potassium dichromate actually dissociates or not. If it does, then it is evident from fig. 3 that dissociation should be complete in the neighbourhood of 450° C; above this temperature it furnishes nearly a straight line.

The following are the observed and calculated values for the viscosities of lead chloride, lead bromide, sodium nitrate, and potassium nitrate. All the observed values are taken from Börnstein Landolt's Table.

Lead chloride.

$\alpha = \bar{2}{\cdot}1334$, $\beta = 80{\cdot}6$, $\theta = 637$.

T.	η (0).	η (c).	Per cent. error.
771	0·05532	0·05551	0·4
791	0·04660	0·04622	0·8
811	0·04020	0·04024	0·1
831	0·03588	0·03588	0·0
861	0·03165	0·03172	0·2
881	0·02956	0·02963	0·2

Lead bromide.

$\alpha = \bar{4}{\cdot}6450$, $\beta = 1507$.

T.	η (0).	η (c).	Per cent. error.
645	0·10190	0·09581	5·0 (!)
665	0·08060	0·08145	1·1
685	0·06970	0·06995	0·4
705	0·06133	0·06057	1·2
735	0·05035	0·04956	1·4
765	0·04075	0·04119	1·0

Sodium nitrate.

$\alpha = \bar{2}{\cdot}4652$, $\beta = 755$.

T.	η (0).	η (c).	Per cent. error.
581	0·02919	0·02919	0·0
601	0·02661	0·02645	0·6
621	0·02439	0·02408	1·3
641	0·02237	0·02207	1·4
671	0·01917	0·01955	2·0
691	0·01828	0·01814	0·8

Potassium nitrate.

$\alpha = \bar{3}{\cdot}0167$, $\beta = 384$.

T.	η (0).	η (c).	Per cent. error.
606	0·02970	0·02989	0·6
626	0·02693	0·02684	0·3
646	0·02442	0·02427	0·6
666	0·02216	0·02208	0·4
676	0·02109	0·02111	0·1
686	0·02007	0·02020	0·6

Summary.

(1) Viscosities of fused sodium nitrate, potassium nitrate, lead chloride, lead bromide, and potassium dichromate have been examined.

(2) In the cases of sodium nitrate, potassium nitrate, and lead bromide, the simple formula $\log \eta = \alpha + \frac{\beta}{T}$ holds good.

(3) In the case of lead chloride a more complex formula, $\log \eta = \alpha + \frac{\beta}{T - \theta}$, is necessary. It is suggested that this is due to the gradual increase in the dissociation of lead chloride with temperature.

(4) In the case of potassium dichromate neither of the two formulæ is applicable at low temperatures. It is suggested that this is due to the decomposition of potassium dichromate into potassium chromate and chromium trioxide.

The Chemical Laboratory,
Ravenshaw College,
Cuttack, India.
Nov. 16, 1932.

XIX. *The Electrophoretic Null-point for Mercury in Aqueous Solutions.* *By* S. R. Craxford *.

IT has long been suspected that the potential of the electrophoretic null-point is closely connected or identical with the so-called absolute zero of potential, or with the electrolytic null-point. The latter is equal to the potential of the electrocapillary maximum in the given solution, and experiments [1] have shown that it agrees with the null-point obtained with the dropping mercury electrode, as would be predicted by the thermodynamical theory of the electrocapillary phenomena [2]. It has also been shown [2] that the electrophoretic force under unit potential gradient, on a small mercury drop, in solutions where the interphase may be regarded as being completely polarizable, is proportional (*a*) to the net electric charge on the drop, or (*b*) to the product of the surface area of the drop with the rate of change of surface tension with potential. If this expression is correct the electrophoretic and electrolytic null-points should coincide, although in general the electrokinetic

* Communicated by O. Gatty, B.A.

potential will not equal the interfacial potential of the drop against the solution.

Electrophoretic experiments have not previously been published for mercury against an aqueous solution when the potential across the interphase is maintained and varied by polarization, and such experiments are described in the present paper for solutions of a number of salts, including cases where specific adsorption of the salt at the interphase is known to occur, so that in this way the potentials of the null-points observed varied over a range of 0·33 volt. In a previous paper [3] it has been shown that the properties of the interphase should in many respects be the same whether the potential across it is fixed by polarization or by the composition of the solution, although, in the latter case, *i. e.*, for a non-polarized interphase, the experimental results are apparently more difficult to interpret. It is of interest, therefore, to consider a certain amount of work that has already been published on the electrophoretic null-point of metals, and more especially of mercury, when the potential across the interphase is controlled by the composition of the solution.

The Electrophoretic Null-point for a Non-polarized Interphase.

J. Billiter observed the electrophoresis of small spheres of platinum, gold, and mercury (the latter in the form of gold amalgam) hanging on quartz-fibres [4] and also of colloid particles of these metals [5], and then prepared "Null Solutions" whose composition was such that the particles did not move in either direction in the applied electric field. By assuming that the potential of the particles against such a solution was the same as that of a macroscopic electrode of the same metal in the same solution, he found the potential of the electrophoretic null-point to be near $\varepsilon_H = +0{\cdot}4$ volt on the normal hydrogen scale. A third method, also developed by Billiter [6], consisted of measuring the potential difference between the ends of a tube of liquid when a metallic powder is allowed to fall through the liquid. The composition of the liquid is again adjusted until this potential becomes zero, and the value for the potential of the electrophoretic null-point is again near $\varepsilon_H = +0{\cdot}4$ volt. But while these results have been confirmed by H. Freundlich and E.

Mäkelt [7] for particles of silver, an equally careful and much more extensive research by H. M. Goodwin and R. B. Sosman [8] using suspended metal spheres, and by W. R. Whitney and J. C. Blake [9] for colloid particles, failed to reveal electrophoretic null-points in this region of potential. These authors conclude that while null-points may occur here in exceptional cases, it is by no means a general phenomenon.

Another series of researches, however, have obtained electrophoretic null-points for mercury near $\varepsilon_H = -0{\cdot}25$ volt. C. Christiansen [10] observed that if mercury drops were allowed to fall through a solution at right angles to an electric field, they were deflected towards the positive or the negative pole according to the composition of the solution. A. Frumkin [11] used this method and prepared null solutions in which the drops suffered no deflexion, and so found the potential of the electrophoretic null-point to be $\varepsilon_H = -0{\cdot}25$ volt. His experiments were done in carefully purified and air-free solutions in a closed apparatus. S. Bodforss [12] also obtained a similar value, $\varepsilon_H = -0{\cdot}12$ volt, by work on the electrophoresis of a large mercury drop resting in a horizontal glass tube filled with a null-solution. This discrepancy between values at $\varepsilon_H = +0{\cdot}4$ volt and values near $\varepsilon_H = -0{\cdot}25$ volt is analogous to the similar discrepancy in the values of the electrolytic null-point when determined for a non-polarized interphase both by the dropping electrode and by the electrocapillary curve methods. This latter discrepancy has been discussed in a previous paper [3], where evidence was adduced to show that it is very probable that the potential of the true electrolytic null-point is near $\varepsilon_H = -0{\cdot}25$ volt. It may be mentioned here that the potentials of the electrophoretic null-point obtained in the present paper for a polarized interphase are also in this region.

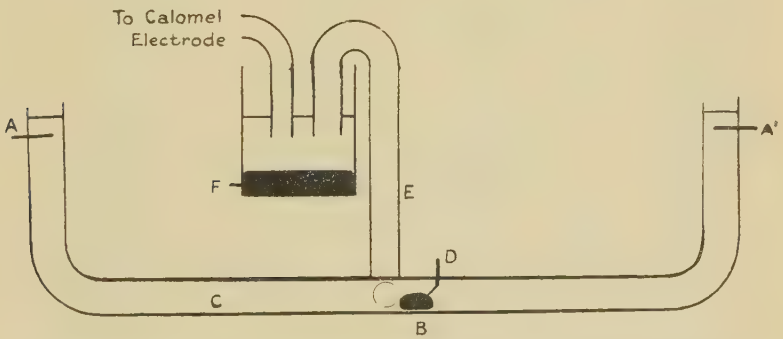
Experimental Method.

If the potential of the drop of mercury whose electrophoresis is observed is to be fixed by polarization, the drop must be connected electrically with an external source of electromotive force. Thus the methods of Christiansen and of Frumkin are unsuitable, so that a modification of Bodforss's method is used. In this method it is only necessary to apply the electric field causing electrophoresis momentarily and to observe the direction

in which the drop kicks, and this is a great advantage over methods that require the continuous application of the field. For in such cases the drop acts as a middle electrode, and the properties of its surface may easily be altered by the products of the resulting electrolysis.

The apparatus used is shown in fig. 1. The field causing electrophoresis is applied through the platinum electrodes A, A′, which are connected through a key to a battery of from 2 to 8 volts. The drop of mercury B is 6 mm. long and rests in the horizontal glass tube C, of diameter about 8 mm. Metallic connexion is made with the drop by the platinum wire D, which just touches it. The side tube E communicates with a flat mercury electrode F, and finally with a saturated calomel reference electrode. The mercury drop is polarized to any

Fig. 1.



desired potential against the solution by applying suitable potentials between D and F, and the potential between D and the calomel electrode is measured. The drop is observed by a microscope magnifying 40 diameters. For each experiment the apparatus is filled with the solution to be investigated, and the polarizing potential applied. On pressing the key to apply the electric field that causes electrophoresis, the drop kicks towards one or other of the electrodes, according to its charge. The polarizing potential is then adjusted until, on repeating this, the drop shows no tendency to move when the field is applied. The electrophoretic null-point is then approached from both sides, and the experiments are then repeated with the electric field reversed. In this way the null-point is enclosed in a bracket normally of width 0·1 volt. At the

null-point the potential of the drop is measured directly against the calomel electrode.

Discussion of the Experimental Results.

The potentials of the electrophoretic null-points so obtained for a series of solutions are given in the table below, where they are compared with the potentials of the corresponding electrocapillary maxima, taken from the work of Gouy [13]. There is a general agreement between the two sets of values, and this is seen more clearly in fig. 2, where the potentials of the electrophoretic null-points are plotted against those of the corresponding electrocapillary

TABLE.

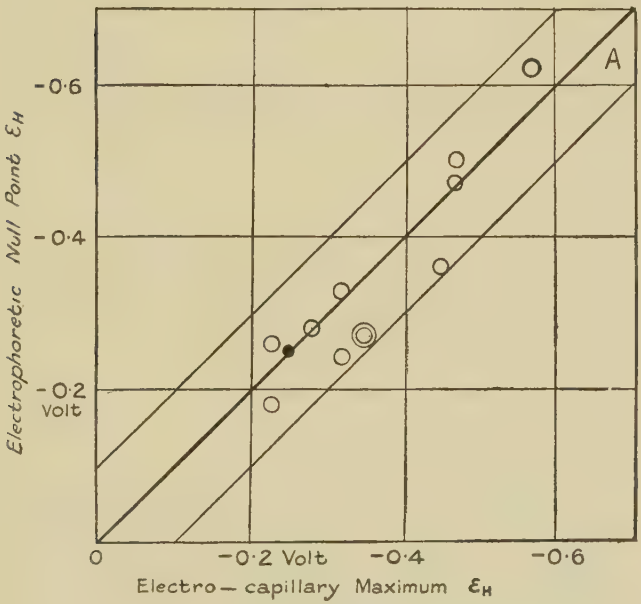
Electrolyte.	Concentration.	Electrophoretic null-point. ε_H.	Electrocapillary maximum. ε_H.
Na_2SO_4	N	−0·26	−0·23
K_2CO_3	N	−0·18	−0·23
KNO_3	N	−0·24	−0·31
KCl	N/2	−0·33	−0·31
KCl	N/10	−0·28	−0·28
KBr	N	−0·36	−0·45
KBr	N/10	−0·27	−0·35
KCNS	N	−0·47	−0·47
KCNS.....	N/10	−0·27	−0·35
KJ	N	−0·62	−0·57
KJ	N/10	−0·50	−0·47

maxima. The theoretical curve obtained by assuming these potentials to be identical is the straight line A, of unit slope. The lines on either side of this indicate the possible experimental error inherent in each of the present measurements, that is, the size of the bracket in which the experimental electrophoretic null-point was enclosed. For comparison the result of Frumkin is included, plotted against the potential $\varepsilon_H = -0{\cdot}25$ for the electrolytic null-point.

The rather crude experimental arrangements used in the present work cause the introduction of various errors, which are of two types. The first, due to such causes as electrolysis through the drop, contact with the platinum wire and with the glass tube will give rise to constant differences between each observation and the true electro-

phoretic null-point. The second, due to the lack of sensitivity of the method, will cause the individual observations to vary about a mean, according to the laws of chance. Each value of the electrophoretic null-point given in the table is the mean of the mid-points of two brackets, and if δ is the difference between these two mid-points, the mean value of this difference is 0·023 volt. The standard deviation of the two, that is, $s_\delta = \sqrt{\frac{\Sigma\delta^2}{10}}$

Fig. 2.



The point shown as ● is due to Frumkin (*loc. cit.*).

for eleven observations, is 0·025 volt. Thus a considerable part of the error in the results is to be ascribed to the insensibility of the method, and so there is justification for using the mean curve about which the results fall.

If, now, Δ is the deviation between any value of the electrophoretic null-point given in the table, and the corresponding potential of the electrolytic null-point, the mean deviation $\Delta = 0{\cdot}02$ volt, the standard deviation

$s_{\bar{\Delta}} = 0{\cdot}055$ volt, and the standard deviation of an observed value for $\bar{\Delta}$ from its true value is 0·2 volt. These figures are consistent with the hypotheses (*a*) that the potentials of the electrophoretic null-point and the electrolytic null-point, as given by the electrocapillary maximum, are the same in all cases, and (*b*) that the deviations between the two fall on a normal error curve.

Summary.

(1) The potential of the electrophoretic null-point for a mercury drop in a series of solutions has been measured, the potential across the mercury-solution interphase being fixed by polarization.

(2) This is found within the limits of experimental error to be the same potential as the electrolytic null-point given by the potential of the electrocapillary maximum in all cases, including those in which salt is strongly specifically adsorbed at the surface of the mercury drop.

Finally, the writer wishes to thank Mr. Oliver Gatty for very valuable help and advice, and also the Department of Scientific and Industrial Research for a grant to enable this work to be carried out.

References.

(1) F. Paschen, *Ann. Phys.* xliii. p. 568 (1891).
(2) S. R. Craxford, O. Gatty, and J. L. St. Philpot. (To be published shortly.)
(3) S. R. Craxford, Phil. Mag. (in the press, same volume as this paper).
(4) J. Billiter, *Z. Elektrochem.* viii. p. 638 (1902).
(5) J. Billiter, Ann. Phys. xi. p. 902 (1903).
(6) J. Billiter, *ibid.* xi. p. 937 (1903).
(7) H. Freundlich and E. Mäkelt, *Z. Elektrochem.* xv. p. 161 (1909).
(8) H. M. Goodwin and R. B. Sosman, Phys. Rev. xxi. p. 129 (1905).
(9) W. R. Whitney and J. C. Blake, J. Amer. Chem. Soc. xxvi. p. 1339 (1904).
(10) C. Christiansen, *Ann. Phys.* xii. p. 1072 (1903).
(11) A. Frumkin, J. Russ. Phys. Chem. Soc. (1) xlix. p. 207 (1917).
(12) S. Bodforss, *Z. Elektrochem.* xxix. p. 121 (1923).
(13) G. Gouy, *Ann. Chim. Phys.* (7) xxix. p. 145 (1903).

The Physical Chemistry Laboratory,
Balliol College and Trinity College,
Oxford.

XX. *Vibration of Piezoelectric Oscillating Crystal.*
By Issac Koga (*Tokyo University of Engineering*) *.

1. FOR several years it has been well known that there is a certain natural vibration of piezoelectric oscillating crystal, the period of vibration being proportional only to the thickness, commonly called "Thickness Vibration." We showed that such a kind of vibration is due to the standing wave produced by interference of plane waves incident on and reflected from the plane boundary surfaces of the medium and verified the theoretical results by several examples, but, since then, as the mathematical expression for the conclusions are considerably improved and one or more of the important properties are obtained, we wish to present them briefly.

2. As has already been dealt with in the previous papers†, to solve the thickness vibration of a very thin crystal plate it is very important to draw attention that the period of vibration is practically dependent upon only the thickness of the plate, that is, is independent of the extent of the principal surfaces of the plate, so that the free vibration of such a kind is what can be realized if these surfaces of the plate extend to infinity.

The free vibration of thin crystal plate having two parallel plane boundary surfaces is due to the interference of plane waves incident on and reflected from those boundary plane surfaces of the medium. In other words, in the thickness vibration of the crystal plate bounded by the two infinite parallel planes the displacement at any point in the medium is dependent only upon the distance from a boundary surface and time. Therefore, if the direction cosines of a normal to the two parallel plane boundary surfaces be l, m, n referred to the rectangular coordinate axes x, y, z, each component of displacement u, v, w at any point is always a function of s and t only, where

$$s=lx+my+nz. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

* Communicated by the Author.

† J. I. E. E. (Japan) Suppl. Issue, 1932, p. 33 ; June 1932, p. 498 ; Physics, vol. iii. August 1932, p. 70.

Thus the general equations of motions in a crystalline medium,

$$\left.\begin{aligned}\frac{\partial X_x}{\partial x}+\frac{\partial X_y}{\partial y}+\frac{\partial X_z}{\partial z}&=\rho\frac{\partial^2 u}{\partial t^2},\\ \frac{\partial Y_x}{\partial x}+\frac{\partial Y_y}{\partial y}+\frac{\partial Y_z}{\partial z}&=\rho\frac{\partial^2 v}{\partial t^2},\\ \frac{\partial Z_x}{\partial x}+\frac{\partial Z_y}{\partial y}+\frac{\partial Z_z}{\partial z}&=\rho\frac{\partial^2 w}{\partial t^2},\end{aligned}\right\}\quad\ldots\quad(2)$$

(the meaning of the letter symbol seems to be superfluous to explain) reduce to the very simple forms :

$$\left.\begin{aligned}\frac{\partial^2}{\partial s^2}(Lu+Hv+Gw)&=\rho\frac{\partial^2 u}{\partial t^2},\\ \frac{\partial^2}{\partial s^2}(Hu+Mv+Fw)&=\rho\frac{\partial^2 v}{\partial t^2},\\ \frac{\partial^2}{\partial s^2}(Gu+Fv+Nw)&=\rho\frac{\partial^2 w}{\partial t^2},\end{aligned}\right\}\quad\ldots\quad(3)$$

where

$$\left.\begin{aligned}&L=P^2,\quad M=Q^2,\quad N=R^2,\\ &F=QR,\quad G=RP,\quad H=PQ,\end{aligned}\right\}$$

and

$$\left.\begin{aligned}P&=lc_1+mc_6+nc_5,\\ Q&=lc_6+mc_2+nc_4,\\ R&=lc_5+mc_4+nc_3,\end{aligned}\right\}\quad\ldots\quad(4)$$

in which c_1, c_2, ... have no quantitative meaning, but in P^2, PQ, ... c_1^2 is to be replaced by c_{11}, c_1c_2 by c_{12}, and so on, c_{11}, c_{12} .... being the adiabatic elastic constants.

Now let ξ be the displacement in the direction λ, μ, ν, then

$$\xi=\lambda u+\mu v+\nu w,\quad\ldots\quad(5)$$

If λ, μ, ν, and c be so chosen that the relations

$$\left.\begin{aligned}\lambda L+\mu H+\nu G&=\lambda c,\\ \lambda H+\mu M+\nu F&=\mu c,\\ \lambda G+\mu F+\nu N&=\nu c,\end{aligned}\right\}\quad\ldots\quad(6)$$

hold, then multiplying the three equations of (3) by

λ, μ, ν respectively and adding together side by side, we get

$$c\frac{\partial^2\xi}{\partial s^2}=\rho\frac{\partial^2\xi}{\partial t^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Eliminating λ, μ, ν between the three equations of (6), we have

$$\begin{vmatrix} L-c & H & G \\ H & M-c & F \\ G & F & N-c \end{vmatrix} =0, \quad . \quad (8)$$

a cubic equation determining c; let its roots, which are proved to be necessarily real and positive*, be c_1, c_2, c_3. When c_1 is substituted in any two of the foregoing equations, the ratios of $\lambda:\mu:\nu$ can be derived; let them be denoted by $\lambda_1:\mu_1:\nu_1$, and suppose the corresponding value of ξ to be ξ_1, with similar expressions for the other values of c. Then ξ_1, ξ_2, and ξ_3 are proved to be always perpendicular to each other.

The solution of (7) is a very simple matter. To determine the normal mode of vibration we must assume that ξ varies as a harmonic function of the time t,

$$\xi \propto e^{ipt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

then as a function of s, ξ must satisfy

$$\frac{d^2\xi}{ds^2}+\frac{p^2\rho}{c}\xi=0, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

of which the complete integral is

$$\xi=A\cos(sp\sqrt{\rho/c})+B\sin(sp\sqrt{\rho/c}), \quad . \quad . \quad . \quad (11)$$

where A and B are independent of s.

Now when both boundary surfaces are free from tractions,

$$\frac{d\xi}{ds}=0 \text{ at } s=0 \text{ and } s=a, \quad . \quad . \quad . \quad . \quad (12)$$

we get

$$B=0 \quad \text{and} \quad \sin(ap\sqrt{\rho/c})=0, \quad . \quad . \quad . \quad (13)$$

from which

$$\frac{p}{2\pi}=\frac{q}{2a}\sqrt{\frac{c}{\rho}}, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

q being integral.

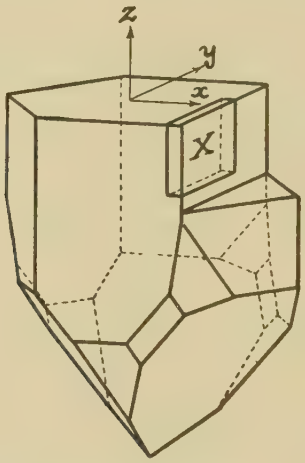
* Lord Kelvin, Baltimore Lectures, London, 1904.

Accordingly, the normal mode of vibration is given by equation of a form

$$\xi = Ae^{ipt} \cos(q\pi s/a). \quad . \quad . \quad . \quad . \quad (15)$$

It is well known that we can excite one or more of the free thickness vibrations by applying an alternating electric field of suitable frequency in the direction normal to the boundary surfaces of crystal, provided the crystal plate is prepared so that it is piezoelectrically active ; and also that it is sometimes possible to sustain a continuous oscillation by properly employing the thermionic tube circuit, the ease of maintenance being considerably

Fig. 1.



dependent upon the medium and the orientation of the boundary surfaces.

3. In quartz, if the coordinate axes be chosen as in fig. 1, the adiabatic elastic constants are given by the following scheme :—

$$\left.\begin{array}{cccccc} c_{11} & c_{12} & c_{13} & c_{14} & 0 & 0 \\ & c_{11} & c_{13} & -c_{14} & 0 & 0 \\ & & c_{33} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 0 \\ & & & & c_{44} & c_{14} \\ & & & & & (c_{11}-c_{12})/2 \end{array}\right\} \quad . \quad (16)$$

therefore the expressions in (4) become

$$\left.\begin{aligned}
\mathrm{L}&=l^2c_{11}+m^2(c_{11}-c_{12})/2+n^2c_{44}+2mnc_{14},\\
\mathrm{M}&=l^2(c_{11}-c_{12})/2+m^2c_{11}+n^2c_{44}-2mnc_{14},\\
\mathrm{N}&=(l^2+m^2)s_{44}+n^2c_{33},\\
\mathrm{F}&=(l^2-m^2)c_{14}+mn(c_{13}+c_{44}),\\
\mathrm{G}&=2lmc_{14}+nl(c_{13}+c_{44}),\\
\mathrm{H}&=2nlc_{14}+lm(c_{11}+c_{12})/2.
\end{aligned}\right\} \quad . \quad (17)$$

By the way, the relations between applied electric field and strains are :

$$\left.\begin{aligned}
-e_{xx}&=d_{11}\mathrm{E}_x, \qquad -e_{zx}=-d_{14}\mathrm{E}_y,\\
-e_{yy}&=-d_{11}\mathrm{E}_x, \qquad -e_{xy}=-2d_{11}\mathrm{E}_y.\\
-e_{yz}&=d_{14}\mathrm{E}_x,
\end{aligned}\right\} \quad . \quad . \quad (18)$$

4. If a quartz crystal be cut by two planes perpendicular to the axis x to obtain a so-called X-cut or Curie-cut quartz oscillating crystal designated by X in fig. 1, the direction cosines of the normal to the principal surfaces is seen to be

$$l=1, \qquad m=n=0. \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Introducing these quantities into (8) and (17), we get

$$\left.\begin{aligned}
c_1&=\mathrm{L}=c_{11},\\
c_2, c_3 \ldots .&\ \text{omitted},
\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (20)$$

and from (6),

$$\lambda_1=1, \quad \mu_1=\nu_1=\lambda_2=\lambda_3=0. \quad . \quad . \quad (21)$$

The displacements ξ are given by

$$\left.\begin{aligned}
\xi_1&=u,\\
\xi_2&=\mu_2 v+\nu_2 w,\\
\xi_3&=\mu_3 v+\nu_3 w,
\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (22)$$

while the electric field in the direction x cannot excite but the displacement u as is seen from (18), so that the frequency of vibration is

$$\frac{p}{2\pi}=\frac{q}{2a}\sqrt{\frac{c_{11}}{\rho}}, \quad . \quad . \quad . \quad . \quad . \quad (23)$$

and the mode of vibration is

$$u=\mathrm{A}e^{ipt}\cos(q\pi x/a), \quad . \quad . \quad . \quad . \quad (24)$$

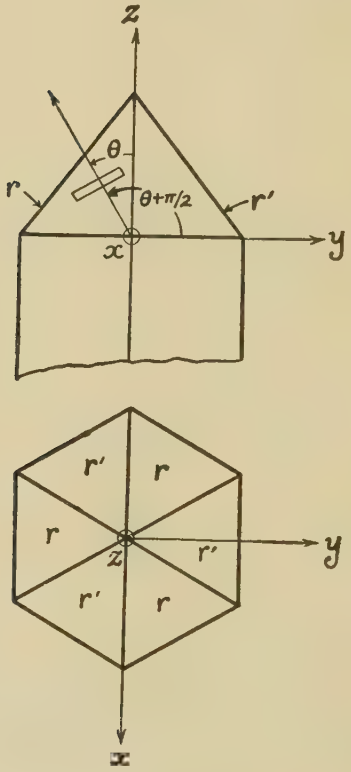
that is, the pure longitudinal vibration along the normal to the boundary surfaces. Numerical examples are not

repeated here as they were already given in our previous papers.

5. In quartz plate cut parallel to the axis x, if the co-latitude of the normal to the principal surfaces be θ as shown in fig. 2, the direction cosines of normal are :

$$l=0, \quad m=-\sin\theta, \quad n=\cos\theta. \quad . \quad . \quad . \quad (25$$

Fig. 2.



Introducing these quantities into (8) and (17), we get

$$\left.\begin{aligned} &c_1=\mathrm{L}=\tfrac{1}{2}(c_{11}-c_{12})\sin^2\theta+c_{44}\cos^2\theta-\mathrm{c}_{14}\sin 2\theta, \\ &c_2,\ c_3 \ldots . \text{ omitted,} \end{aligned}\right\}. \quad (26)$$

and from (6),

$$\lambda_1=1, \quad \mu_1=\nu_1=\lambda_2=\lambda_3=0. \quad . \quad . \quad . \quad (27)$$

The displacements ξ are given by

$$\left.\begin{aligned}\xi_1&=u,\\ \xi_2&=\mu_2 v+\nu_2 w,\\ \xi_3&=\mu_3 v+\nu_3 w,\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (28)$$

of which ξ_2 and ξ_3 cannot be excited piezoelectrically by the electric field in the direction of normal to the principal surfaces, because the z-component of the applied electric field is inactive, while the y-component cannot excite but the pure shears $\partial u/\partial z$ and $\partial u/\partial y$, as is clear from (18) and (28), so that the frequency and normal modes of vibration are given by

$$\frac{p}{2\pi}=\frac{q}{2a}\sqrt{\frac{c_1}{\rho}}, \quad . \quad . \quad . \quad . \quad . \quad (29)$$

and

$$u=\mathrm{A}e^{ipt}\cos\left(q\pi\frac{-y\sin\theta+z\cos\theta}{a}\right), \quad . \quad . \quad (30)$$

which shows that the vibration is always of a pure shear regardless of θ. By the substitution

$$\theta=\phi+\tfrac{1}{2}\arctan\frac{-2c_{14}}{c_{44}-\frac{1}{2}(c_{11}-c_{12})}, \quad . \quad . \quad . \quad (31)$$

we get

$$c_1=\tfrac{1}{2}\{c_{44}+\tfrac{1}{2}(c_{11}-c_{12}) +\sqrt{\{c_{44}-\tfrac{1}{2}(c_{11}-c_{12})\}^2+4c^2{}_{14}}\cos 2\phi\} \quad . \quad (32)$$

Fig. 3 gives the value c_1 for various values of θ or ϕ, employing the numerical values given by W. Voigt *, dots in the figure being the values $(pa)^2\rho/(\pi q)^2$ by actual measurements.

6. In quartz, X-cut plate is the only one that can realize the pure longitudinal thickness vibration piezoelectrically. For, if the thickness vibration be longitudinal, there must be the relations

$$\lambda=l, \qquad \mu=m, \qquad \nu=n, \quad . \quad . \quad . \quad (33)$$

or introducing in (6), the three equations

$$\left.\begin{aligned}&l(l^2+m^2)c_{11}+ln^2(c_{13}+2c_{44})+6lmnc_{14}=lc,\\ &m(l^2+m^2)c_{11}+mn^2(c_{13}+2c_{44})+3n(l^2-m^2)c_{14}=mc,\\ &n(l^2+m^2)(c_{13}+2c_{44})+n^3c_{33}+m(3l^2-m^2)c_{14}=nc,\end{aligned}\right\} \quad . \quad (34)$$

must hold simultaneously.

* 'Lehrbuch der Kristallphysik,' 1923, s. 754, u. 789.

Fig. 3.

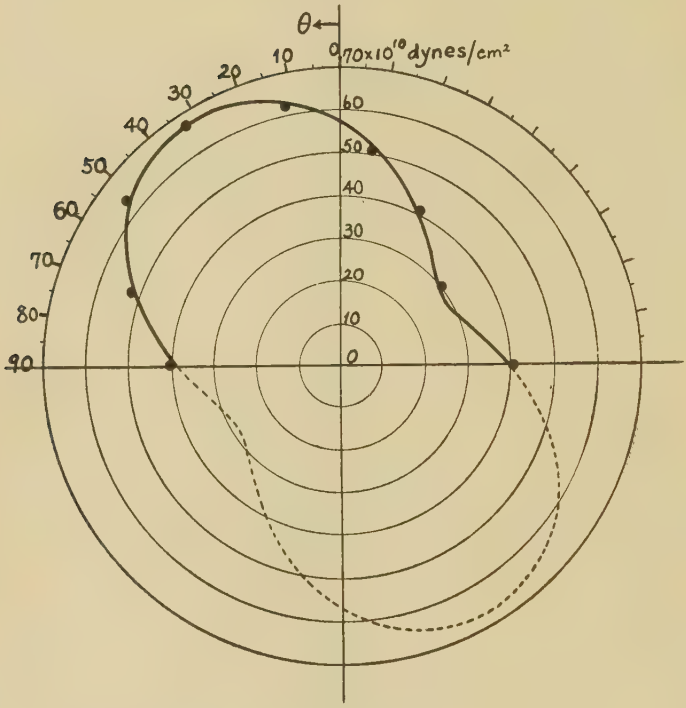
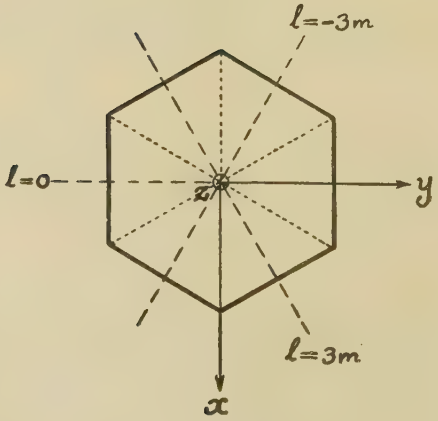


Fig. 4.



From the first two relations, we get

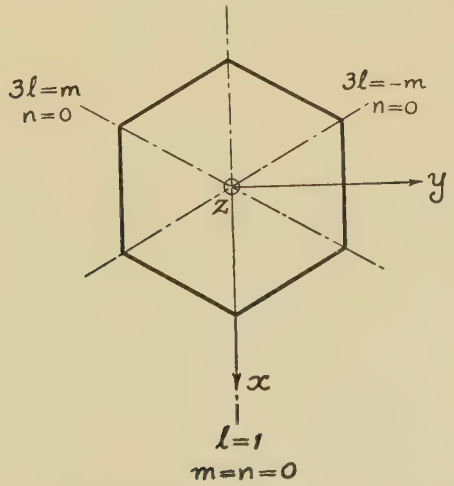
$ln(l^2-3m^2)=0$, *i. e.*, $l=0$, $l^2=3m^2$, or $n=0$, . (35)

but, remembering that the axis z is the trigonal axis, $l=0$ and $l^2=3m^2$ indicates that the direction is in the plane perpendicular to the electrical axis as shown in fig. 4, so that longitudinal vibration cannot be realized as is shown in the last section, while $n=0$ together with the last relation of (34) gives

$$m(3l^2-m^2)=0, \quad i.\,e., \quad m=0 \quad \text{or} \quad 3l^2=m^2, \ . \quad (36)$$

which shows that the direction is in coincidence with the electrical axis as shown in fig. 5, so the vibration is able to be excited piezoelectrically as is discussed in the fourth section.

Fig. 5.



Thus the X-cut or the Curie-cut plate is the only one that can realize the pure longitudinal thickness vibratiou.

7. *Summary.*

Normal modes and frequency of thickness vibration are given in the mathematical expressions, and the special problems about the quartz plates are dealt with. In quartz, the X-cut plate is the only one that can realize the longitudinal thickness vibration. Plates cut parallel to the electrical axis vibrate always in the pure shear mode.

XXI. *A Graphical Method for determining the Transit Times of Electrons in a Three-electrode Valve under Conditions of Space-charge Limitation.* *By* J. S. McPetrie, *B.Sc., A.M.I.E.E.* (*The National Physical Laboratory*)*.

Abstract.

When a thermionic valve is used to produce electronic oscillations, the frequency of these is dependent upon the transit times of the electrons between the valve electrodes. In the following paper a graphical method is described by which these transit times may be determined for electrons under conditions in which the current is limited by the space-charge.

Introduction.

Tonks and Gill [1], [2] have suggested that electronic oscillations are obtained from a three-electrode valve with high positive potential on the grid only when the current in the grid-anode space is limited by space-charge. The period of the oscillations is then assumed to be equal to the time of transit of the electrons from the grid to the anode and back again to the grid, instead of the total time from filament to anode and back to the filament as required by the ordinary theory of Barkhausen and Kurz [3].

In the following paper a graphical method is described by which the interelectrode transit times under space-charge limited current conditions may be determined.

Interelectrode Transit Times when Space-charge is negligible.

In the Barkhausen and Kurz theory, the effect of space-charge on the potential distribution, and, therefore, the interelectrode transit times of the electrons, is neglected. Scheibe [4] has given the complete analysis of the time of transit in this case for the three-electrode valve with cylindrical electrodes. His result for the time

* Communicated by R. L. Smith-Rose, Esq.

of transit of an electron from the filament to grid of such a valve is given by

$$t_{fg}=\frac{2r_g}{\sqrt{\frac{2eV_g}{m}}}f\left(\sqrt{\log_e\frac{r_g}{r_f}}\right), \quad . \quad . \quad . \quad . \quad (1)$$

in which r_f and r_g are the radii of the filament and grid respectively, and V_g is the potential of the grid with respect to the filament.

The similar equation giving the time from the grid to the position in the grid-anode space at which the electron reverses its direction of motion is

$$t_{ga}=\frac{2r_g}{\sqrt{\frac{2eV_g}{m}}}g\left(\sqrt{\frac{V_g}{V_g-V_a}\log_e\frac{r_a}{r_g}}\right), \quad . \quad . \quad (2)$$

in which r_a is the radius of the anode, and V_a its potential with respect to the filament. When V_a is zero, equation (2) reduces to

$$t_{ga}=\frac{2r_g}{\sqrt{\frac{2eV_g}{m}}}g\left(\sqrt{\log_e\frac{r_a}{r_g}}\right). \quad . \quad . \quad . \quad (3)$$

In these equations the functions $f(x)$ and $g(x)$ have the form

$$f(x)=xe^{-x^2}\int_0^x e^{u^2}du$$

and

$$g(x)=xe^{x^2}\int_0^x e^{-u^2}du.$$

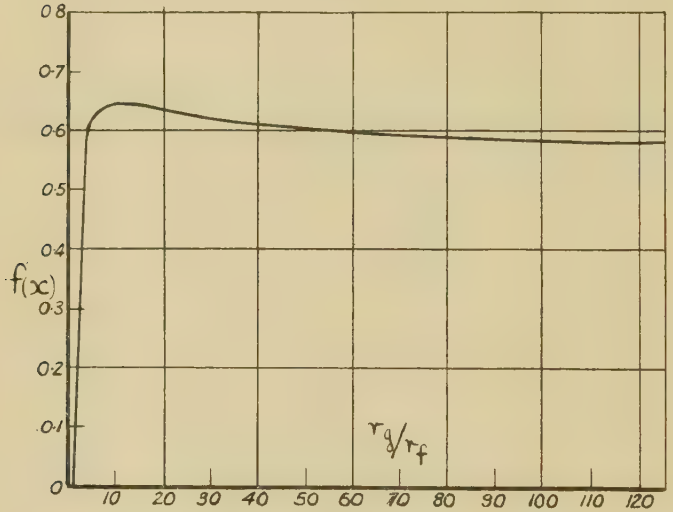
The values of $f(x)$ and $g(x)$ (the latter when $V_a=0$) for different values of r_g/r_f and r_a/r_g are given in figs. 1 and 2.

The values of $f(x)$ and $g(x)$ are determined for the condition when the effect of space-charge distribution within the valve is negligible. The determination of the inter-electrode transit times for any density of space-charge is difficult, but the maximum times when the grid-filament and grid-anode spaces are assumed to be carrying their maximum electronic current are readily determined by the graphical method described below.

Time of Transit from Filament to Grid when Current in Grid-filament Space is limited by Space-charge.

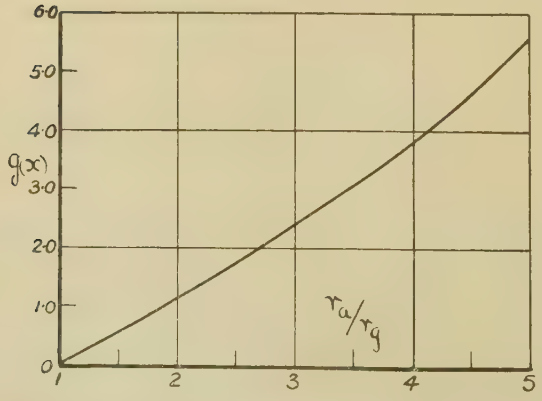
Langmuir [5] has shown that in a diode the maximum current, in amperes, which can pass from one centimetre

Fig. 1.



The relation of the function $f(x)$ to the ratio of the radii of grid and cathode.

Fig. 2.



The relation of the function $g(x)$ to the ratio of the radii of anode and grid.

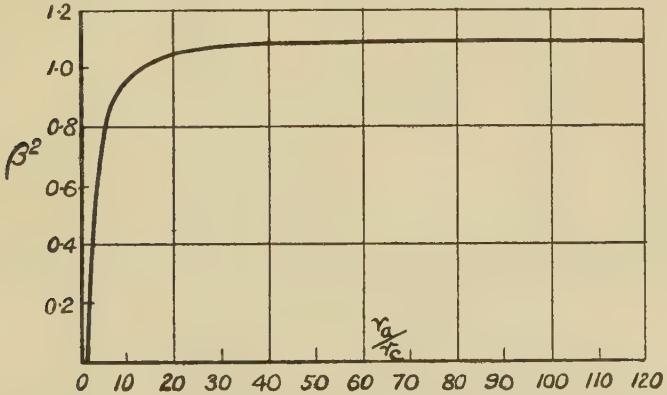
length of an internal filament to an external cylindrical anode is given by the expression

$$i = \frac{14{\cdot}65 \times 10^{-6} \times V^{3/2}}{\beta^2 r_a}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which V is the potential difference between the filament and anode expressed in volts, r_a is the radius of the anode in cm., and β is a function of the ratio of the filament and anode radii. The value of β^2 for different values of this ratio is given in fig. 3.

Langmuir's analysis can be applied to the filament-grid space of a triode with a positive grid voltage and carrying

Fig. 3.



The relation of β^2 to the ratio of the radii of cathode and anode, when the anode is external to the cathode.

the electronic current limited by the space-charge so as to determine the interelectrode transit time, since this space is equivalent to a cylindrical diode with external anode represented by the grid of the triode. The current across the interelectrode space is constant, so that the potential at any radial distance from the filament can be determined from equation (4), when r_a is replaced by this radial distance, and β_r^2 has the corresponding value of that function. For any value of r, therefore, the appropriate value of β_r^2 can be determined from fig. 3, and so the potential throughout the space is given by equation (4), which reduces in this case to

$$V_r^{3/2} \alpha \beta_r^2 r. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

But the velocity at any point within the valve is given by the well-known relation

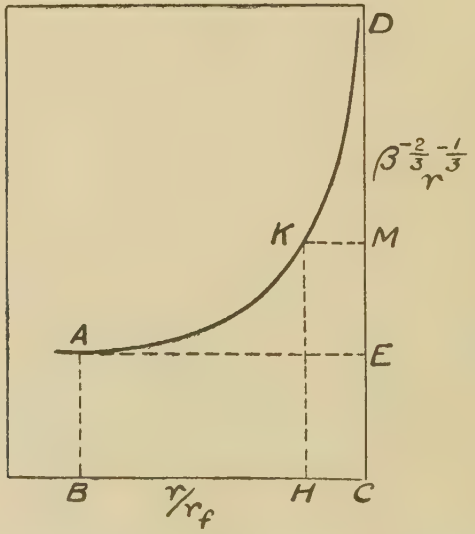
$$v = \sqrt{\frac{2eV}{m}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Equations (5) and (6) combine to give the relation

$$v_r \alpha \beta_r^{2/3} r^{1/3}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Suppose for a given valve with filament of radius r_f a

Fig. 4.



curve is drawn in which $1/v_r$ is plotted as ordinate against the corresponding value of the ratio r/r_f as abscissa. For the grid-filament space of a triode with positive grid a curve is obtained similar to that shown in fig. 4.

Now the time of transit of the electrons between any two points in the grid-filament space is given by the value of

$$\int \frac{dr}{v},$$

taken between the two points as limits. The value of this integral is proportional to the area which the curve

in fig. 4, between the ordinates representing the two points considered, makes with the axis of abscissæ.

Suppose the positions of the grid and filament are represented by the ordinates AB and CD respectively Then the area of the curve ABCD is proportional to the time of transit of the electrons from the filament to the grid of the valve considered. If the velocity of the electrons was uniform throughout the grid-filament space and equal to that at the grid, the time of transit would be represented on the same scale by the rectangular area ABCE. The velocity at the grid, however, is equal to $\sqrt{\frac{2eV_g}{m}}$, where V_g is the potential of the grid. The distance between the filament and grid is $r_g - r_f$. The area ABCE, therefore, represents a time of

$$\frac{r_g - r_f}{\sqrt{\frac{2eV_g}{m}}} \text{ seconds.}$$

Hence the area ABCD represents a time of transit from filament to grid under space-charge limited current conditions of

$$\frac{\text{Area ABCD}}{\text{Area ABCE}} \times \frac{r_g - r_f}{\sqrt{\frac{2eV_g}{m}}} \text{ seconds.}$$

Relation (7) is quite general, so that it gives the distribution of velocity throughout any diode. Fig. (4) can, therefore, be applied to determine the time of transit in any given diode by selecting the ordinate AB representing the position of the anode (the grid of the triode in the case under consideration) of the diode.

Scheibe's values of $f(x)$ can now be altered to give the appropriate values of that function for space-charge limited current conditions. Let this function be called $F(x)$. Scheibe's value for the transit time between the filament and grid is

$$t_{fg} = \frac{2r_g}{\sqrt{\frac{2eV_g}{m}}} f(x).$$

The corresponding time under space-charge limited current conditions is

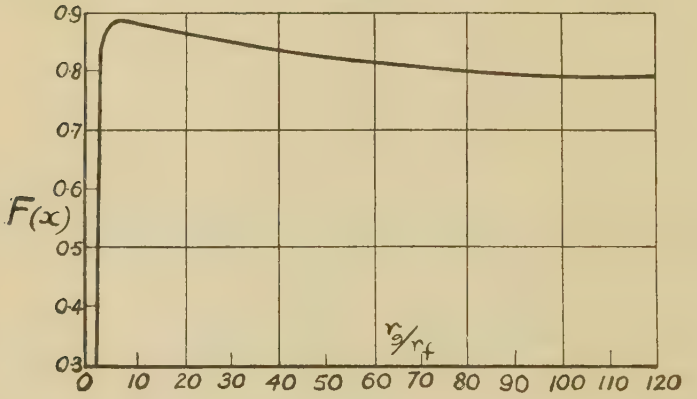
$$\frac{\text{Area ABCD}}{\text{Area ABCE}} \frac{r_g - r_f}{\sqrt{\frac{2eV_g}{m}}} = \frac{2r_g}{\sqrt{\frac{2eV_g}{m}}} \mathrm{F}(x).$$

Therefore

$$\mathrm{F}(x) = \frac{\text{Area ABCD}}{\text{Area ABCE}} \frac{r_g - r_f}{2r_g}.$$

The values of $\mathrm{F}(x)$ for different values of r_g/r_f are given in fig. 5.

Fig. 5.



The area ABCD in fig. 4 for any given value of r_g/r_f can readily be determined by planimeter or any other method of graphical integration. It will be observed that the curve is asymptotic to the ordinate representing the position of the filament, and it might be suggested that the graphical integration of the curve near this ordinate would be impossible. At such positions, however, the radii of the grid and filament are very nearly equal. Under this condition the two electrodes may be considered plane. It can be shown that when this is the case the transit time of the electrons between the filament and grid is exactly three times what it would be if the velocity of the electrons was uniform throughout the grid-filament space, and everywhere equal to that at the grid. This means that in the

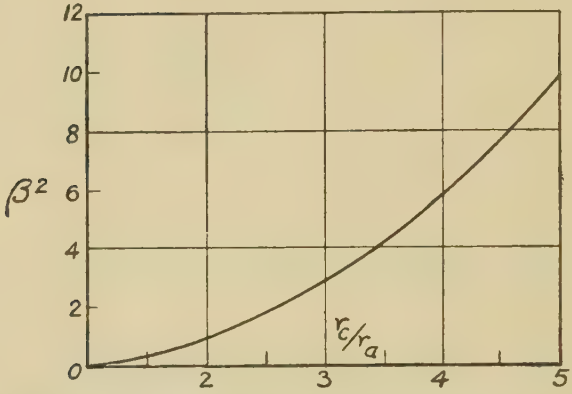
limit when AB approaches very near to CD, the area ABCD becomes approximately three times that of the rectangular area ABCE. The area ABCE can be calculated accurately so that the area ABCD is determined. To find the area of the curve ABCD when AB is not close to CD, the planimeter need only be used up to a convenient ordinate (say HK) and three times the rectangular area HCMK added to the result.

Time of Transit from Grid to Anode when Current in Grid-anode Space is limited by Space-charge.

In a triode with a positive potential on the grid the electrons emitted from the filament reach the grid with a high velocity. A certain proportion escape into the grid-anode space, where they experience a retarding field if the anode is at a potential lower than that of the grid. If the potential of the anode is lower than that of the filament the electrons cannot reach the anode but return to the grid. As the filament emission is increased the number of electrons entering the grid-anode space increases, and if the filament emission is increased sufficiently, a condition may be reached under which no more electrons can enter the grid-anode space. In this case the current in the grid-anode space is limited by space-charge and a virtual cathode is formed near the anode. The grid-anode space can then be represented by an equivalent diode having a filament at the virtual cathode and an anode represented by the grid of the triode. Langmuir has shown that for a diode with external cathode equation (4) is still applicable, but that in this case the value of β^2 is a different function of the ratio of the anode and cathode radii. The new values of β^2 are shown graphically in fig. 6.

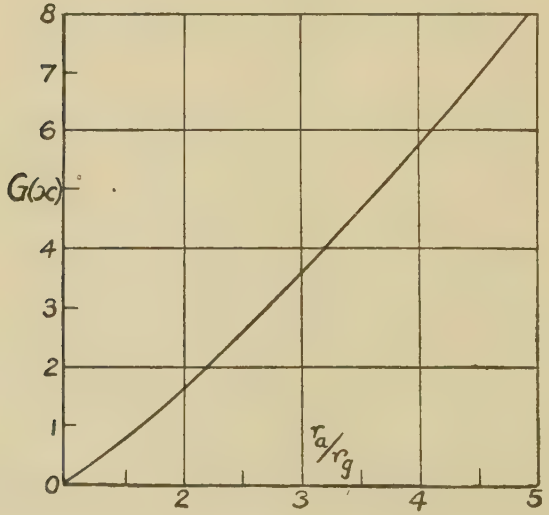
The graphical method for determining the time of transit in the grid-anode space is exactly the same as that for the grid-filament space and need not be described at any length. The curve corresponding to fig. 4 is similar, so that the reasoning given for the grid-filament space applies directly to the present case if the radius of the filament is altered to the radius r_a of the virtual cathode in the grid-anode space. If the anode voltage is equal to that of the filament, the value of r_a is that of the radius of the anode. For this case, if the

Fig. 6.



The relation of β^2 to the ratio of the radii of cathode and anode, when the cathode is external to the anode.

Fig. 7.



form of equation (3) is preserved and the time of transit from grid to anode is made equal to

$$\frac{2r_g}{\sqrt{\frac{2e\overline{V}_g}{m}}}\,G(x),$$

G(x) has the values shown graphically in fig. 7.

Limitations in the Accuracy of Determination of the Transit Time.

Three assumptions are made in Langmuir's analysis of the space-charge current in a diode. They are :

(1) That the cathode is an equipotential surface ;

(2) that the velocity of emission from the filament is zero, and

(3) that both anode and filament are infinitely long, so that there are no end effects.

When the anode potential of the diode is high compared with the potential drop along the filament, the error due to the first assumption becomes negligible. Under the same condition the errors due to the other assumptions should not materially alter the time of transit of the electrons from the filament to the anode of the diode.

Conclusions.

The graphical method described above is suitable for the determination of the interelectrode transit time when the current is limited by space-charge. Whether this is the condition under which electronic oscillations are obtained is a matter which is not under consideration in the present paper, and one which requires further investigation.

The work described in this paper has been carried out as part of the programme of the Radio Research Board, and acknowledgment is due to the Department of Scientific and Industrial Research for granting permission for publication. The author is also indebted to Mr. H. M. Bristow for assistance in the computations involved.

References.

(1) L. Tonks, Phys. Rev. xxx. p. 501 (1927).
(2) E. W. B. Gill, Phil. Mag. xii. p. 843 (1931).
(3) H. Barkhausen and K. Kurz, *Phys. Zeits.* xxi. p. 1 (1920).
(4) A. Scheibe, *Ann. der Phys.* lxxiii. p. 54 (1924).
(5) I. Langmuir, Phys. Rev. ii. p. 450 (1913).

XXII. *An X-Ray Investigation of the Gold-Rhodium and Silver-Rhodium Alloys.* *By* Roy W. Drier, *B.S., E.M., E. Met., M.S., Assistant Professor of Metallurgy, and* Harold L. Walker, *B.S., M.S., Instructor in Metallurgy, Michigan College of Mining and Technology**.

IN 1900 Rössler found what he thought to be pure crystals of rhodium in gold upon cooling a melt of rhodium and gold †. He also stated that silver would not dissolve rhodium, and, in fact, that the solidified melt indicated insolubility in the liquid state.

More definite and accurate conclusions as to solubility are possible by present-day methods; it was therefore determined to check the findings of Rössler by measurement of the contraction or enlargement of the space-lattices as indicated by X-ray diffraction patterns.

Preparation.

The materials used were of as high a degree of purity as was obtainable commercially. The gold and the rhodium were purchased as C. P. metals; the silver was 999·75 fine. An arc spectrum of the rhodium did not show the presence of any of the other platinum metals. The X-ray spectrum of the rhodium gave the value of a_0 as 3·799 Å., which is in good agreement with the values listed by Knaggs, Karlich and Elam in 'Tables of Cubic Crystal Structure' (1932). The spectrum of silver gave the value of 4·077 Å. for a_0; that of the gold was taken from the 'International Critical Tables' as 4·070 Å.

The fact that rhodium when melted in the presence of charcoal dissolves carbon up to 7 per cent.‡ eliminated the oxy-acetylene method for fusion. Since the sample was too small to provide enough resistance to cause fusion, the induction furnace was also eliminated. It might have been possible to use carbon crucibles for the resistance and small MgO crucibles to hold the sample, except that the MgO crucibles were not impervious to carbon vapour.

* Communicated by the Authors.
† Guertler, 'Metallographie,' 1912, p. 116.
‡ *Comptes Rendus*, 1911, pp. 153, 814.

A hydrogen-rich oxy-hydrogen flame was consequently found to be most practicable. The alloys were melted in quartz tubing and quartz crucibles.

Each sample weighed approximately 200 mg. Because of volatilization (presumably of the gold, for in places the crucibles had a coloration of rose gold) the final button weighed less than the sum of the initial components. The greatest loss occurred in the high gold alloys and amounted to as much as 7 per cent.

After fusion and solidification each button was cooled gradually by moving it into the cooler hydrogen-rich part of the flame until, after 5 minutes of such an annealing treatment, its temperature was approximately 500° C., too low for any oxide formation. About half of the button was then removed by filing, the filings being used for X-ray diffraction, and the remaining half being polished, etched, and examined microscopically. The etchants used were sodium cyanide plus ammonium persulfate, aqua regia, and potassium bisulfate.

Microscopic examinations were conducted with magnifications up to 800 diameters. The difficulty encountered in etching these noble metals militated against fine differentiation between phases, particularly with very small concentrations, but never were any more than two phases present. In the gold-rhodium system the rhodium phase tended to crystallize out in dendritic form.

Before raying, the filings were annealed for approximately 20 hours in a nitrogen atmosphere at temperatures just below the sintering-point. 860° C. was sufficient to sinter a 75 per cent. (by weight) gold sample. The higher rhodiums sintered at higher temperatures.

The annealed filings were screened through 200-mesh bolting cloth, were placed in a pyrex tube of 0·4 mm. internal diameter, and were rayed in a General Electric Diffraction Unit using slits 0·2 mm. and 0·4 mm. wide. Both gold and rhodium were used as comparators. Molybdenum K radiation was used in obtaining the spectra ; both Ka_1 and Ka_2 were used in their translation. The films were placed in the General Electric semi-logarithmic scale, and a cathetometer was used to standardize the film according to the particular comparator employed. The cathetometer could be read to 0·001 cm., which would correspond to approximately 0·0001 Å. in the vicinity of interplanar spacings of 1 Å. on the scale,

though this degree of accuracy was not attained throughout.

The unit parameter of the alloy was determined by two methods—first by direct readings of the scale, and then by a reading of the difference between the spectrum line of the standard and the line of the alloy. This distance was then evaluated in Å. for that particular part of the scale; the per cent. ratio of this change to the total change possible indicated the solubility. By this latter method such sources of error as changes in film length, possible impurities in the metals used, and question as to the standard cell size of the alloying elements, had very little effect on the final determinations.

Method of Computation.

a=actual distance between spectral line of standard and corresponding line in the alloy.

b=value in cm. of ·01 Å. of that part of the G. E. scale where spectral line is located.

c=relative interplanar spacing for line read.

d=difference in Å. between a_0 of standard and alloy.

f=total possible difference in a_0 for a 100 per cent. change in composition.

$$\frac{\left(\frac{a}{b}\times\cdot 01\text{ Å.}\right)}{c}=d.$$

If Vegard's additive law obtained in the case of these alloys, $\frac{d}{f}$ would equal the atomic solubility. However, Westgren and Almin * have proved, for the systems Cu–Al, Ag–Al, and Ni–Al, that the atomic solubility is not a straight line function of the unit parameter, but that the a_0, and consequently the volume per atom, follow a curve expressing a_0 to a power less than 1. In this present investigation the solubilities in the Au–Rh and the Ag–Rh systems have been computed as though the alloys followed Vegard's law. These solubilities thus really represent the minimum limits of total solubility of gold or silver in rhodium, and the maximum limits of solubility of rhodium in gold or silver.

* A. Westgren and A. Almin, *Zeit. für Phys. Chem.* Band 5, Heft 1, pp. 18–28 (1929).

Discussion.

The difficulties encountered in preparing samples—extremely high temperatures, volatilization, and spitting—made it impossible to prepare them with the accuracy necessary for the plotting of the solubility-a_0 curve.

The samples prepared showed the maximum enlargement of the unit parameter of rhodium to be 0·003 Å. According to Vegard's law this would indicate a solubility of 1·1 atomic per cent. of gold in rhodium. A sample with 2·5 atomic per cent. gold showed the same increase, which would mean that the lower limit of solubility was 1·1 per cent. and that the higher possible limit was below 2·5 per cent. Westgren's and Almin's results would indicate a probable solubility of 1·5 atomic per cent.

The maximum contraction of the gold lattice due to the dissolving of rhodium amounted to 0·011 Å. According to Vegard's law this lattice change would indicate a solubility of 4·1 atomic per cent. rhodium in gold. A sample with 8·9 atomic per cent. of rhodium showed the same change in unit parameter, which would indicate a solubility somewhere between 4·1 and 8·9 atomic per cent. If we again use Westgren's and Almin's curves and realize that rhodium has an electron defect similar to that of nickel, it is quite probable that the true solubility is nearer the higher than the lower limit

These two solid solution phases were the only ones found throughout the whole system, which apparently is one of two limited solid solutions. J. N. Friend * mentions a gold-rhodium alloy containing 30–43 per cent. rhodium. Samples of this analysis showed only the spectra of the two solid solutions.

Silver-Rhodium Series.

No definite limits for the solubility of silver in rhodium could be established, but some of the spectra examined indicated a possible solubility of the order of magnitude of 0·1 atomic per cent. No solubility of rhodium in silver was found.

Micrographs and X-ray spectra showed the presence of only two phases throughout the whole system. It is improbable that absolute insolubility of either silver or

* J. N. Friend, 'Text-book of Inorganic Chemistry,' vol. ix. part i. pp. 154–5.

rhodium in each other obtains ; and it is quite probable that this system, like the gold-rhodium system, is composed of two solid solutions, the solubility on either end of the system being exceedingly slight.

Summary.

The gold-rhodium system was found to be one of two solid solutions. The gold lattice contracted a maximum of 0·011 Å., which, according to Vegard's law, indicates a solubility of 4·1 atomic per cent. of rhodium in gold. Limiting spectra and consideration of Westgren's and Almin's findings indicated that a better value for this solubility would be nearer to 8 than to 4 atomic per cent. The edge of the unit cell of rhodium expanded as much as ·003 Å. Similar considerations would indicate the solubility of gold in rhodium to be between 1·1 and 2·5 atomic per cent., with the possibility of its being nearer 1·5 atomic per cent.

The solubility of silver in rhodium or rhodium in silver could not be detected, but theoretical considerations make it probable that these two are at least minutely soluble in each other and that this system, too, is one of two exceedingly limited solid solutions.

The authors wish to acknowledge their appreciation of aid and encouragement extended to them by Professor A. T. Sweet, head of the Department of Metallurgy and Ore Dressing of the Michigan College of Mining and Technology, and to Professor Lars Thomassen of the University of Michigan.

XXIII. *An Empirical Equation for calculating Osmotic Pressures.* *By* the Rt. Hon. the Earl of Berkeley, *F.R.S.**

Part I.—Application to Non-Ionized Solutions.

In a letter to 'Nature' (June 29th, 1929) it was shown that a simple expression, the factors of which are physical constants of the solution, will give the osmotic

* Communicated by the Author.

pressures of aqueous solutions of sugar-like substances, provided the osmotic pressure at one concentration is known. Since that letter was published several formulæ which remove the restriction just mentioned have been found. The following, although fitting the results slightly less well than others, is given because some of its factors are amenable to a plausible explanation *.

The formula is

$$Pws_2/A^{2/3}(e^{A^{1/3}}-1) = K, \text{ a constant}, \quad . \quad . \quad (1)$$

where P is the osmotic pressure, w the specific volume of the solution.

$$A = \frac{c_2 s_2}{c_1 s_1} \times \frac{M_1}{M_2},$$

where $c_2 = 1 - c_1$ is the number of grammes of solute in 1 gramme of solution; s_2 and s_1 are the changes in the volume of a practically infinite mass of solution when 1 gramme of solute or solvent (respectively) is withdrawn; M_2 and M_1 are the molecular weights of solute and solvent.

The s's are calculated from the two equations

$$s_1 = w - c_2\, \partial w/\partial c_2 \quad \text{and} \quad s_2 = w - c_1\, \partial w/\partial c_1,$$

which are derived from $w = c_2 s_2 + c_1 s_1$; and the specific volume w has, wherever possible, been corrected for the compressibility of the solution.

Tables I. and II. give the data for calculating the constant at 0° C. and 30° C. for aqueous solutions of cane-sugar, α methyl glucoside, and one or two other substances; the headings of the columns explain themselves sufficiently; the osmotic pressures at 0° C. up to 134 atmos. are directly observed, while above that pressure they are derived from measurements of the lowering of the vapour pressure. At 30° C. they are all of the latter category.

Remarks on Tables I. and II.

It should be noted that the lower osmotic pressures are subject to greater percentage error both in the direct method and in that obtained from the lowering of vapour pressure; but it is clear that the formula represents the lower pressures with fair accuracy.

In some cases the densities of more dilute solutions are given, although the corresponding osmotic pressures have not

* The equation $Pw^2/A(1-\frac{1}{2}A^{2/3}+\frac{1}{4}A^{4/3}) = $ a constant is quite a good fit, but preference is given to (1) because it contains no arbitrary constants.

Table I.

At 0° C.

Reference number.	c_2.	P, in atmospheres.	Density of uncompressed solution.	w.	s_1.	s_2.	A.	$e^{A^{1/3}}-1$.	$\frac{Pws_2}{A^{2/3}(e^{A^{1/3}}-1)} = K$.	Remarks.
				Cane sugar. $M_2=342{\cdot}18$.						
(1)	0·03289	2·23	1·01326	0·98691	1·0002	0·6008	0·001078	0·1080	1164	* (11) & (12) Cane-sugar are derived from the lowering of vapour pressure.
(2)	0·09243	6·85	1·03813	0·96327	0·9997	0·6052	0·003246	0·1596	1141	
(3)	0·17030	14·21	1·07205	0·93279	0·9991	0·6099	0·006598	0·2063	1110	
(4)	0·23435	21·87	1·10134	0·90798	0·9983	0·6130	0·009897	0·2395	1100	† (2) & (3) Isodulcite are derived from the lowering of vapour pressure (unpublished). The direct osmotic pressures are reported by Berkeley and Hartley (Proc Roy. Soc. cxii. p. 486 (1916)) to be too low owing to leakage through the membrane.
(5)	0·25343	24·55	1·11032	0·90064	0·9980	0·6139	0·010996	0·2491	1101	
(6)	0·36102	43·91	1·16329	0·85832	0·9941	0·6181	0·01849	0·3026	1085	
(7)	0·44812	67·43	1·20910	0·82529	0·9904	0·6219	0·02685	0·3491	1106	
(8)	0·52830	100·53	1·25357	0·79549	0·9839	0·6273	0·03759	0·3979	1123	
(9)	0·58506	134·86	1·28669	0·77452	0·9801	0·6288	0·04763	0·4369	1144	
(10)	0·64664	186·86	1·32383	0·75207	0·9746	0·6304	0·06233	0·4867	1158	
(11)	0·68504	230·70 *	1·34771	0·73827	0·9689	0·6323	0·07472	0·5238	1159	
(12)	0·70845	264·46 *	1·36259	0·72986	0·9651	0·6331	0·08393	0·5495	1160	

α Methyl glucoside. $M_2 = 194{\cdot}11$.

(1)	0·25926	48·29	1·09319	0·91309	0·9967	0·6743	0·02202	0·3235	1170
(2)	0·31034	64·22	1·11341	0·89611	0·9956	0·6751	0·02833	0·3565	1172
(3)	0·35484	80·50	1·13149	0·88143	0·9942	0·6764	0·03474	0·3858	1168
(4)	0·39024	96·17	1·14619	0·86981	0·9928	0·6776	0·04054	0·4099	1172
(5)	0·42857	115·74	1·16243	0·85728	0·9911	0·6788	0·04768	0·4370	1172
(6)	0·47368	142·46	1·18195	0·84262	0·9889	0·6801	0·05751	0·4711	1163
(7)	0·51219	170·18	1·19896	0·83009	0·9866	0·6812	0·06729	0·5019	1158

Isodulcite. $M_2 = 164{\cdot}10$.

(1)	0·04408	N.D.	1·01512	0·98511	1·0000	0·6622			
(2)	0·23705	47·2 †	1·08700	0·91996	1·0000	0·6624	0·02260	0·3267	1152
(3)	0·26292	54·5 †	1·09744	0·91121	1·0001	0·6620	0·02594	0·3445	1140

Glucose. $M_2 = 180{\cdot}10$.

(1)	0·18553	29·17 ‡	1·07797	0·92767	0·9985	0·6177	0·01410	0·2733	1062
(2)	0·28510	53·19 ‡	1·12350	0·89008	0·9965	0·6231	0·02495		
(3)	0·38462	87·87 ‡	1·17188	0·85333	0·9944	0·6276	0·03947		
(4)	0·45596	121·18 ‡	1·20877	0·82729	0·9930	0·6298	0·05320		

Glycerine. $M_2 = 92{\cdot}06$.

	0·25379	90·72 §	1·065	0·9684	0·9947	0·7526	0·05035	0·4467	1096

‡ (1), (2), (3), & (4) Glucose The sugar contained some methyl alcohol (Berkeley and Hartley, Phil. Trans. Roy. Soc. ccvi. p. 497 (1906)) which passes through the membrane and so causes the measured osmotic pressure to be too low. The higher the pressure the greater the divergence.

§ Glycerine. This number is derived from the lowering of the vapour pressure and is unpublished.

The mean value of K

for Cane-sugar is	1138
α Methyl glucoside	1168
Isodulcite	1496
Glycerine	1614
The weighted mean .	6110

Table II.

At 30° C.*

Reference number.	c_2.	P, in atmospheres.	Density of uncompressed solutions.	w.	s_1.	s_2.	A.	$e^{A^{1/3}}-1$.	$\frac{Pws_2}{A^{2/3}(e^{A^{1/3}}-1)} = K$.	Remarks.
				Cane-sugar.						
(5)	0·25373	26·82	1·10173	0·90676	1·0026	0·6248	0·01116	0·2505	1214	
(6)	0·36102	47·25	1·15271	0·86616	1·0005	0·6284	0·01869	0·3039	1202	
(7)	0·44812	72·59	1·19712	0·83349	0·9976	0·6313	0·02706	0·3502	1210	
(8)	0·52830	107·55	1·24055	0·80372	0·9938	0·6340	0·03761	0·3979	1227	
(9)	0·58506	143·33	1·27278	0·78284	0·9890	0·6366	0·04780	0·4374	1240	
(10)	0·64664	198·89	1·30909	0·76032	0·9820	0·6392	0·06271	0·4878	1255	For Cane-sugar the mean value of K is 1232.
(11)	0·68504	249·16	1·33251	0·74626	0·9772	0·6401	0·07502	0·5247	1275	
				α Methyl glucoside.						
(1)	0·25926	49·42	1·08399	0·92086	1·0013	0·6915	0·02244	0·3259	1207	
(2)	0·31034	65·14	1·10308	0·90450	1·0005	0·6911	0·02886	0·3589	1204	
(3)	0·35484	81·73	1·12017	0·89029	0·9990	0·6926	0·03540	0·3843	1238	
(4)	0·39024	96·75	1·13407	0·87904	0·9879	0·6932	0·04127	0·4128	1196	
(5)	0·42857	115·34	1·14942	0·86689	0·9961	0·6942	0·04850	0·4399	1194	
(6)	0·47368	141·66	1·16788	0·85269	0·9944	0·6952	0·05840	0·4740	1173	For α Methyl glucoside the mean value of K is 1208.
(7)	0·51219	168·34	1·18399	0·84065	0·9911	0·6974	0·06859	0·5058	1163	
				Isodulcite.						
(1)	0·04408	N.D.	1·00948	0·99061						
(2)	0·23728	49·84	1·07820	0·92747	1·0059	0·6753	0·02293	0·3285	1177	For Isodulcite the mean value of K is 1169.
(3)	0·26292	57·26	1·08816	0·91898	1·0062	0·6746	0·02625	0·3461	1161	
				Glycerine.						
(1)	0·12442	39·30 †	1·02483	0·97577	1·0043	0·7756	0·02148	0·3205	1201	For Glycerine the mean value of K is 1169.
(2)	0·25402	95·74 †	1·057	0·9461	1·0040	0·7770	0·05159	0·4511	1126	

* All the osmotic pressures are derived from the lowering of the vapour pressure.

† These osmotic pressures are not yet published.

The weighted mean value of K is 1209.

been determined—they help in calculating correct values for s_2 and s_1.

The constants for glycerine are somewhat low. The vapour density experiments from which the osmotic pressures are calculated are not yet published, but it may here be stated that, as there seems to be no criterion by which the purity of the substance can be tested, it was assumed to be pure when redistilled with air under reduced pressure (about 1 cm. Hg).

In the case of dextrose the direct osmotic pressures were derived from the sugar contaminated by alcohol. Subsequently the substance was freed from the alcohol by recrystallization, and its solution subjected to a vapour pressure determination, which, however, was not a very successful experiment.

At first it might be thought that there is no sufficient reason for taking the specific volume of the compressed solu-

TABLE III.

Substance.	A 0° C.	At 30° C.	Ratio.
Cane-sugar	1138	1232	1·08
Methyl glucoside	1168	1196	1·02
Isodulcite	1146	1169	1·02
Glycerine	1096	1169	1·07
Weighted mean	1146	1209	1·06

tion, for the maximum difference between compressed and uncompressed is that for the most concentrated cane-sugar solution, and is only of the order of 1 per cent.* ; but as there are solutions or liquid mixtures of very great osmotic pressures, where the compression effect is probably over 10 per cent. and where the calculated s's may well diverge still further, it seemed better at the outset to emphasize the theoretical aspect, namely. that the physical constants involved should be those of the solution under the conditions of the experiment (or, in the case of vapour pressure determinations, under the conditions contemplated in the definition of osmotic pressure).

Table III. gives the mean values of K for the different substances (excluding the glucose results) at 0° C. and 30° C. It will be seen that the figures are within 5 per cent. of the mean value. The ratios are surprisingly small, but as the definition of osmotic pressure is the difference between the pressures on the solution and solvent when both are

* The ratio s_2/s_1 may diverge more.

at the same temperature, it is obvious that no direct comparison can be made between the osmotic pressures at two different temperatures. In other words, a solution at 0° C. separated by a membrane from one of the same concentrations at 30° C., each being under pressures equal to their osmotic pressures, would not in general be in equilibrium—nor would two samples of the solvent be in equilibrium when under the same pressure * but at two different temperatures—the Soret effect. Obviously, if the magnitude of the Soret effect were known, the change in osmotic pressure with temperature can be calculated.

It seems possible that further experiments with other solvents in conjunction with those with water might enable both the Soret effect and the temperature coefficient of osmotic pressure to be calculated.

As the equation contains the molecular weight of the solute and the solvent specifically, it may afford a means of testing the molecular structure of either component; and if it be found to apply to ionized solutions, a correction to the usual formula for the freezing-point determination of molecular weight may be required.

Obviously by combining Prof. Porter's formula for determining osmotic pressures from the lowering of the vapour with equation (1) a connexion between RT and K will emerge and the vapour pressure of any solution can be calculated provided that of the pure solvent is known; but this does not seem worth pursuing until the equation is more firmly established.

The Meaning of s_1 and s_2.

Prof. Porter † defines s_1 as the change in the volume of a practically infinite mass of solution when 1 gramme of solvent is withdrawn. Similarly for s_2. It is clear that these quantities are functions of c_2 and P and the temperature T; by analogy with the specific volume of a solution which is also a function of c_2, P, and T, s_1 and s_2 may be called the specific volume of the solvent or the solute *in the solution* when the latter is at concentration c_2, pressure P, and temperature T.

A little consideration of what may take place when substances are dissolved or are mixed together will show that the term "specific volume" as used above might be misleading. For greater ease in presenting this problem s_1

* Even without neglecting the difference in vapour pressures.

† Proc. Roy. Soc. A, lxxix. pp. 519, 520 (1907).

may be defined as the change in volume when 1 gramme of the solvent is *added* to a practically infinite volume of the solution ; similarly for s_2.

Without attempting great accuracy it may be stated that all solutions and mixtures can be placed in one or other of the following categories, which are differentiated from one another by the consideration of what may happen to the 1 gramme when it is added as above :—

(1) If the whole of it combines chemically or otherwise with the solute, and the solution remains liquid, we can say that s_1 *is* the specific volume of the solvent in the solution.

(2) If none of it combines with the solute, and is neither associated nor dissociated, again s_1 *is* the specific volume of the solvent in the solution, despite the fact that there may be a general shrinkage *.

(3) If part of the gramme be associated or dissociated †, s_1 will no longer be the specific volume, but will represent an average value, which, when the corresponding mean molecular weight be used, will give a mean value for the constant of equation (1).

(4) If *part* of the gramme combines with the solute, neither s_1 nor s_2 can be regarded as specific volumes.

Meaning of the Quantities in Equation (1).

Although the equation is empirical, yet, as there are no arbitrary constants, it may have some physical meaning.

For instance, if put in the form

$$\mathrm{P}ws_2 = 1146\frac{\mathrm{A}(e^{\mathrm{A}^{1/3}}-1)}{\mathrm{A}^{1/3}}$$

and $e^{\mathrm{A}^{1/3}}-1$ be expanded, it can be said that the osmotic pressure P is proportional to A and to the series

$$1+\frac{\mathrm{A}^{1/3}}{2}+\frac{\mathrm{A}^{2/3}}{6}+,$$

* It would seem that the solutions considered in Tables I. and II. come under this category, so that both s_1 and s_2 are the respective specific volumes.

† Solutions of ionized salts may come under this category.

or, multiplying in by A, P is proportional to A plus a series beginning with the term $\frac{A^{4/3}}{2}$*.

Now, taking s_1 and s_2 as the "specific" volume of the solvent and solute (respectively) when in the solution, A is the ratio of the volume of the molecules of solute to the volume of the molecules of the solvent, while the terms in $A^{4/3}$ will represent the square and other powers of the ratio of their areas.

It is possible to give an explanation of the appearance of A and $A^{4/3}$ on the "defect in internal pressure" theory of osmotic pressure, but before doing so a word as to the usual objection to this theory may not be out of place. The objection lies in the fact that the volume of a solution is, in the vast majority of cases, smaller than the sum of the volumes of its components; and it is argued that this shrinkage can only be due to a greater internal pressure. If it is remembered that equilibrium across a semipermeable membrane can only obtain when the number of solvent molecules going in one direction are balanced by an equal number going in the opposite direction †, it is clear that the "internal pressure" under discussion should refer only to the *solvent*, whether in the solution or not; hence the "internal pressure" of the solution, which includes the attractions of the *solute* molecules to one another, is *ultra vires*.

Incidentally it may be pointed out that on solution a redistribution of the solvent molecules may occur such that they are further apart (and therefore their mutual attractions are lessened), and yet the sum of the separate volumes of solvent and solute may be greater than the resulting total volume.

The defect in internal pressure theory says that osmotic pressure is caused by the lowering of the internal pressure of the solvent by the presence of the solute. If we assume that the solute takes no part in the bombardment of the

* Attention should be drawn to the magnitude of the term $\frac{A^{4/3}}{2}$; the highest numerical value is for cane-sugar at 0°, where A = ·0839; so that $\frac{A^{4/3}}{2}$ = ·0184 is approximately 25 per cent. of A; and the next term is only ·003 or 4 per cent. of A: hence to the degree of accuracy aimed at, it is easy to see that the first two or three terms of a number of series could be found to replace the one under discussion.

† Or more exactly, when the masses passing in the two directions are equal and carry the same total energy, *i. e.*, kinetic energy together with any energy there may be of association or combination.

membrane, then it is easy to see that the defect in the internal pressure will be (1) proportional to the volume of the solute, and (2) inversely proportional to the volume of the solvent; for in (1) the solute displaces a number of solvent molecules in proportion to its volume and in (2) the number displaced is inversely proportional to the volume of the solvent. But there is a further effect to be added, in that the solute molecules are themselves bombarded by the solvent, and if, as it is now generally thought to be, there is a definite interval of time (the "rest" period) during which the molecules remain in contact, a further number of solvent molecules are withdrawn from bombarding the membrane; this effect is proportional to the area of the solute molecules, and as the solute molecules themselves make excursions to and fro they will capture and embrace some solvent, an effect also proportional to the area, and so we may assume the two effects proportional to the square of this area. But it is difficult to see how the number of solvent particles engaged in a "rest period" can be inversely proportional to their own areas, and it may turn out that the equation is in this respect incorrect; of course it is possible that some sort of screening effect of the solvent molecules on each other takes place and accounts for the inverse proportionality, but until the equation is tested in solutions other than aqueous and it is found to hold (or not) it seems unnecessary to speculate further.

The appearance of s_2 as a factor on the left-hand side of the equation is so far inexplicable; it serves, however, to reduce the equation for dilute solutions to

$$Pw^2 = \frac{c_2 M_1}{c_1 M_2},$$

and for dilute aqueous solutions to

$$P = \frac{c_2 M_1}{c_1 M_2}.$$

Both osmotic pressures of mixtures of ethyl alcohol and water have been calculated from the vapour pressure determination of Dobson (J. C. S. cxxvii. p. 2866), using Moesveld (Landolt and Börnstein) compressibilities. The osmotic pressures with alcohol as *solute* give values of K of the equation

$$Pws_a/A^{2/3}(e^{A^{1/3}}-1) = K,$$

which, for the more concentrated mixtures, are completely different from those given in Table II., even if they be

calculated on the assumption that the alcohol is associated with double molecules in the mixture. Nor can the values of K for the osmotic pressures with alcohol as *solvent* be brought to equality. These calculations are based on Prof. Porter's thermodynamic cycle (Proc. Roy. Soc. lxxx. p. 457 (1908)) for mixed volatile liquids.

The solutes hitherto discussed are all of the alcohol type of molecule. It would be expected therefore that, anyhow as far as the osmotic pressures of ethyl alcohol dissolved in water are concerned, the equation would give values of K approximating to 1200 (the value for 25° C.); but as this is not so, it may not be out of place to suggest reasons for the discrepancy.

As the value of K for the strongest alcoholic mixture given by Dobson is about 100 (only 8 per cent. of the expected number) it is probable that there is a fundamental error somewhere. An explanation of this may be that alcohol and water combine both in the mixed liquid and in the vapour—if this be so, then two consequences emerge: (1) s_1 and s_2 are no longer the "specific" volumes of solvent and solute, (2) Dobson's partial pressures are not the true partial pressures, and therefore Prof. Porter's formula is not applicable.

Part II.—Application to Ionized Aqueous Solutions.

As already pointed out in Part I. (p. 305) it is probable that s_1 and s_2 can be taken as the mean "specific" volume of the solvent and solute in solutions of salts, and it is permissible to apply equation (1) thereto, provided the mean molecular weights are also used.

If, however, combination between water and salt (or ions) does, in fact, take place, then the physical meaning given to the equation fails; nevertheless it seems worth while using the equation in its empirical character in hopes that it will throw some light on the dissociation question.

Table IV. gives the results for those salts* the physical constants of which have been determined with sufficient accuracy. It should be remembered that the compressibilities of the solutions are required, especially for high osmotic pressure, if the values of s_1 and s_2 are to be calculated to within 5 per cent.

The columns in the table give the same factors as before, but another column, headed M_2', is added. M_2' is the mean molecular weight of the salt (ionized and non-ionized) calcu-

* The dearth of suitable material is astonishing.

TABLE IV.

At 0° C.

Reference number.	c_2.	P, in atmospheres.	Density of uncompressed solution.	w.	s_1.	s_2.	A.	$e^{A^{1/3}}-1$.	$\frac{Pws_2}{A^{2/3}(e^{A^{1/3}}-1)} = K$.	M_2'.	Number of ions.	Remarks.
					Calcium ferrocyanide. $M_2 = 292{\cdot}6$.							
(1)	0·02902	2·54	1·02472	0·97588	1·000	0·1788	0·000329	0·07145	1303	258	1·7	Experiments (2), (3), and (4) give $M_2' > M_2$. This is strongly indicative of association. The number of ions at infinite dilution is therefore that for the double molecule.
(2)	0·06605	5·34	1·05716	0·94593	0·999	0·2023	0·000882	0·1007	1109	304		
(3)	0·10884	9·20	1·09592	0·91248	0·996	0·2267	0·001712	0·1264	1052	320		
(4)	0·14973	14·65	1·13444	0·88149	0·993	0·2474	0·002700	0·1493	1104	304		
(5)	0·17907	20·33	1·16287	0·85994	0·990	0·2624	0·003569	0·1651	1190	281·5		
(6)	0·23890	41·22	1·22322	0·81651	0·977	0·3055	0·006046	0·1998	1535	218		
(7)	0·28317	70·84	1·26858	0·78683	0·969	0·3229	0·008106	0·2225	2004	171		
(8)	0·30016	87·09	1·28661	0·77557	0·962	0·3406	0·009352	0·2345	2203	155·8		
(9)	0·32074	112·84	1·30860	0·76218	0·957	0·3495	0·01062	0·2458	2531	134·2		
(10)	0·33270	131·00	1·32106	0·75473	0·952	0·3591	0·01158	0·2540	2730	127·5		
					Strontium ferrocyanide. $M_2 = 387{\cdot}15$.							
(1)	0·05837	3·39	1·05302	0·94965	0·9996	0·1480	0·000427	0·0793	1059	412	2·2	Here all the values of M_2' are greater than M_2. The ions are those of the single molecule salt. No stress should be laid on the decrease in the M_2' of (5); the change is too small.
(2)	0·11119	5·98	1·10470	0·90522	0·9970	0·1735	0·001013	0·1057	880	501		
(3)	0·11902	6·38	1·11314	0·89836 *	0·9967	0·1757	0·001109	0·1091	861	513		
(4)	0·15233	8·59	1·14690	0·87192	0·9956	0·1854	0·001558	0·1229	841	524·5		
(5)	0·19351	12·04	1·19253	0·83855	0·9951	0·1847	0·002073	0·1360	844	522		
					Magnesium ferrocyanide. $M_2 = 258{\cdot}9$.							
(1)	0·05754	6·20	1·05128	0·95122	0·9964	0·2112	0·000901	0·1015	1316	226		
(2)	0·07787	8·70	1·06873	0·93569	0·9940	0·2451	0·001450	0·1197	1301	228·5		
					Potassium ferrocyanide. $M_2 = 368{\cdot}3$.							
(1)	0·01496	2·93	1·01050	0·98961	1·0000	0·2989	0·000222	0·0624	3790	113	3·7	Unfortunately there are no data for calculating M_2' for highly concentrated solutions. It is possible that M_2' might reach a maximum which would show whether this salt is associated or not.
(2)	0·02936	5·41	1·02086	0·97957	0·9997	0·3149	0·000466	0·0806	3441	124·5		
(3)	0·05331	9·19	1·03773	0·96364	0·9988	0·3391	0·000935	0·1028	3055	140·7		
(4)	0·08170	13·52	1·05810	0·94509	0·9979	0·3559	0·001552	0·1228	2762	155·8		
(5)	0·11956	19·45	1·08575	0·92102	0·9960	0·3792	0·002530	0·1460	2503	172		
					Sodium ferrocyanide. $M_2 = 303{\cdot}9$.							
(1)	0·02214	5·33	1·01751	0·98279	1·0000	0·2384	0·000320	0·0708	3771	93·8	4·1	The preceding remarks apply also to this salt.
(2)	0·03412	7·84	1·02704	0·97367	0·9947	0·2405	0·000504	0·0829	3497	101·4		
(3)	0·04823	10·69	1·03828	0·96313	0·9988	0·2533	0·000762	0·0956	3272	108·6		
(4)	0·06545	14·21	1·05203	0·95054	0·9979	0·2742	0·001141	0·1102	3079	115·4		
(5)	0·08227	17·69	1·06554	0·93849	0·9970	0·2878	0·001535	0·1222	2941	121·2		
					Methyl ferrocyanide. $M_2 = 272{\cdot}0$.							

& Methyl ferrocyanide. $M_2 = 272{\cdot}6$.												
(1)	0·06807	5·96 †	1·01843	0·98190	0·9996	0·7442	0·00360	0·1657	1118	278		Had there been no leak through the membrane K would have been greater (and M_2' lower); it is probable therefore that the evidence for association is not trustworthy.
(2)	0·36918	52·32 †	1·10632	0·90390	0·9965	0·7474	0·03217	0·3744	933	331		
Calcium ferrocyanide. $M_2 = 544{\cdot}0$.												
(1)	0·01945	2·56	1·01312	0·98705	0·9999	0·3389	0·0002221	0·0624	3746	169·3	4·0	
(2)	0·02559	3·23	1·01729	0·98300	0·9999	0·3410	0·0002967	0·0690	3529	179·2		
(3)	0·06281	8·68	1·04292	0·95885	0·9994	0·3538	0·0007857	0·0967	3577	178·0		
(4)	0·09203	14·33	1·06374	0·94008	0·9990	0·3598	0·001209	0·1124	3803	168·5		
Potassium ferrocyanide. $M_2 = 329{\cdot}2$.												
(1)	0·03912 ‡	7·58	1·0224 ‡	0·97809	0·9998	0·4455	0·000993	0·1050	3160	152·6	3·4	The number of ions at infinite dilution is but a very rough approximation. There is only one experiment on dilute solutions.
(2)	0·16248	32·39	1·09649	0·91200	0·9952	0·4831	0·005154	0·1885	2538	121·7		
(3)	0·21881	47·61	1·13195	0·88343	0·9936	0·4899	0·007560	0·2169	2467	157·5		
Magnesium camphorate. $M_2 = 242{\cdot}43$.												
(1)	0·04171	5·91 †	1·02247	0·97802	0·9982	0·5138	0·001815	0·1298	1537	121·2		
(2)	0·07850	N.D.	1·03993	0·96160								
Sodium chloride §. $M_2 = 58{\cdot}46$.												
(1)	0·003445	2·384	1·0025	0·99645	0·9999	0·2306	0·0002457	0·0646	2162	31·2	2·0	Evidently the salt is completely dissociated at infinite dilution. The maximum M_2' of (8) and the subsequent decreases of (9) and (10) may be fortuitous, as their differences are less than 5 per cent.
(2)	0·003748	2·545	1·0027	0·99635	0·9999	0·2306	0·0002674	0·0665	2118	31·9		
(3)	0·006262	4·194	1·0047	0·99523	0·9998	0·2347	0·0004561	0·0800	2067	32·7		
(4)	0·025800	17·50	1·0197	0·98000	0·9985	0·2618	0·002140	0·1376	1962	34·7		
(5)	0·028286	19·13	1·0216	0·97818	0·9983	0·2650	0·002382	0·1429	1944	34·8		
(6)	0·059469	42·89	1·0456	0·95483	0·9957	0·2980	0·005831	0·1972	2061	35·65		
(7)	0·068249	50·06	1·0525	0·94825	0·9949	0·3065	0·006956	0·2104	1897	35·90		
(8)	0·096364	75·32	1·0742	0·92820	0·9918	0·3275	0·010855	0·2478	1885	36·3		
(9)	0·11369	94·91	1·0877	0·91620	0·9854	0·3423	0·01373	0·2706	1918	35·75		
(10)	0·21335	238·1	1·1670	0·8377	0·9742	0·3968	0·03400	0·3826	1970	35·05		

* The concentrations and specific volumes of (2) and (3) are too close together to give a proper value for the s_1 and s_2 of (3). These are therefore calculated from the values of (2) and (4).

† These osmotic pressures are slightly too low owing to leaks through the membranes.

‡ Both derived from graph of densities and concentrations.

§ The osmotic pressures are calculated from Smit's determinations of vapour pressures and from Schumann's compressibilities; both in Landolt and Börnstein.

lated from the equation by assuming that $M_1 = 18{\cdot}02$; then by successive approximation a value M_2' is found which makes $K = 1146$.

There are two noteworthy observations to be made : (1) for all dilute solutions the value of M_2' decreases with dilution ; (2) in the case of calcium ferrocyanide M_2' reaches a maximum and then steadily decreases with increased concentration ; while signs of this phenomenon are shown by strontium ferrocyanide, calcium ferrocyanide, and sodium chloride.

Evidently (1) represents the increase of ionization with increased dilution. If, then, M_2' be plotted against c_2, and its value when $c_2 = 0$ be divided into M_2, the result will be a rough approximation* to the number of ions at infinite dilution. The number of ions are given in the last column of the table.

The fact that the number of ions at infinite dilution for NaCl comes out to be about two seems to give some confidence in the equation, for here the curve is nearly linear and more weight attaches to the extrapolation.

Attention should be drawn to the maximum value of M_2' in the cases of calcium, strontium (and methyl ?) ferrocyanides ; it is greater than M_2, and therefore ionized double molecules are probably involved.

An explanation of the phenomena under (2) is hard to find. There seems to be two possibilities : (*a*) that association between the water and the salt takes place, in which case s_1 and s_2 are no longer the "specific" volumes of the solvent and solute in the solutions, but some function of this volume, which, in the present state of our knowledge, cannot be evaluated ; or (*b*) that just as increased dilution causes a progressive increase in the ionization of the salt, increased concentration will cause a progressive change in the molecular weight of the water. It may be that the following objection to (*b*) will be raised.

Berkeley, Hartley, and Burton† determined the osmotic pressures of concentrated calcium ferrocyanide solutions both by direct measurement and by the method of vapour pressure lowering. The resulting osmotic pressures agreed to about 1 per cent., and as in the latter method RT, which enters as a factor, involves the molecular weight of water vapour, this vapour then cannot be altered to any considerable extent by the hypothetical change in the molecular

* Unfortunately the necessary data (osmotic pressures at high dilutions) for a more accurate extrapolation are wanting.

† Phil. Trans. Roy. Soc. A, vol. ccviii. pp. 295–345.

weight. The objection can be met by the assumption that these aqueous molecules are but slightly volatile.

Incidentally the objection just mentioned can also be raised against (*a*), and is to be met by the reply that the association of water with salt results in molecules which are involatile.

XXIV. *The Magnitude of the* L-*Absorption Discontinuities.* *By* Ivor Backhurst, *M.Sc., Physics Department, National Physical Laboratory, Teddington, Middlesex* *.

IT has been established by E. Jönsson [1] that the ratio of the two absorption coefficients at the K-discontinuity is equal to the ratio of the corresponding atomic energy levels. It was also suggested by him that a similar relation might hold for the total L-absorption jump, *i. e.*,

$$J(L_1/M_1)=E_1/E, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

E_1 and E being the values of the L_1 and M_1 energy levels respectively. An investigation by the writer [2] shortly afterwards on gold and platinum tended to confirm this relation as well as to suggest the following equalities :—

$$J(L_2/M_1)=2^{-\frac{1}{4}}(E_2/E), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$J(L_3/M_1)=2^{-\frac{1}{2}}(E_3/E), \quad . \quad . \quad . \quad . \quad . \quad (3)$$

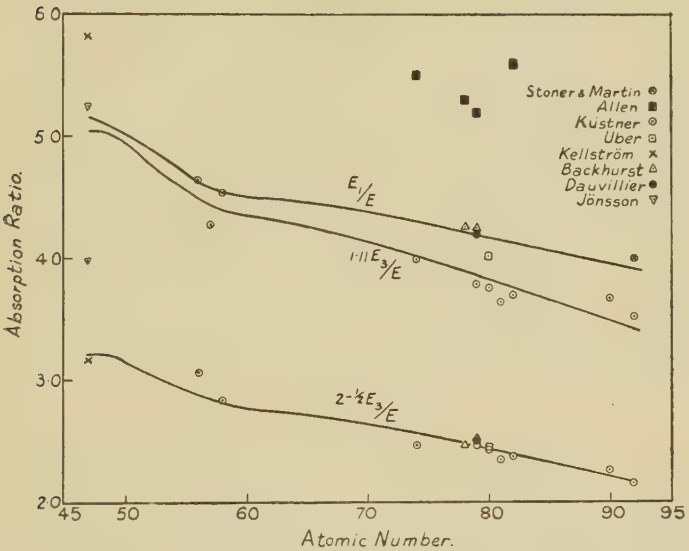
where E_2 and E_3 are the values of the L_2 and L_3 energy levels respectively. At the time, data were available for too small a number of elements to test these equations, but further data, due to Uber [3] and Küstner [4], are now available and, in the absence of an adequate theoretical treatment of the subject, it may be of value to examine to what extent equations of this kind hold good.

All the available results obtained by X-ray measurement, of which description has been given, are contained in figs. 1 and 2 and in the table. The values, due to Küstner, are deduced from measurements of his diagrams [4]. The energy level ratios have been obtained from figures given by Siegbahn [5]. From fig. 1, it is seen that experimental results for the (L_3, M_1) jump are in quite good agreement with equation (3). Incidentally, the experimental accuracy for $J(L_3/M_1)$ is likely to be

* Communicated by Dr. G. W. C. Kaye, O.B.E.

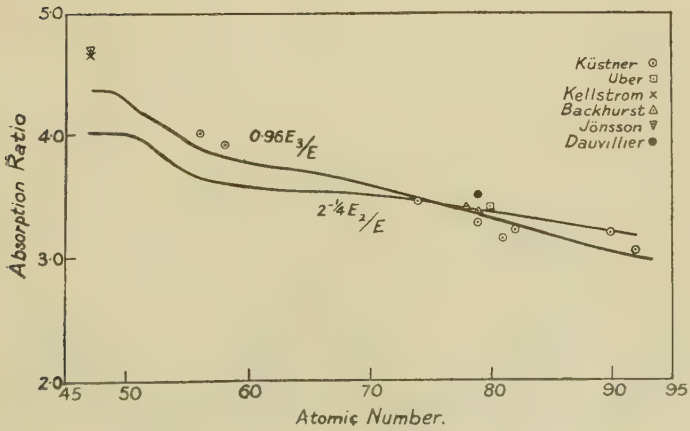
higher than that for $J(L_2/M_1)$ or $J(L_1/M_1)$, as it is easier to determine.

Fig. 1.



Comparison of energy level ratios, indicated by continuous curves, with L-absorption jump ratios.

Fig. 2.



Comparison of energy level ratios, indicated by continuous curves, with L-absorption jump ratios.

Element.	Author.	$J(L_1/M_1)$.	E_1/E.	Per cent. diff.	$1{\cdot}11E_3/E$.	Per cent. diff.	$J(L_2/M_1)$.	$2^{-\frac{1}{4}}E_2/E$.	Per cent. diff.	$0{\cdot}96E_6/E$.	Per cent. diff.	$J(L_3/M_1)$.	$2^{-\frac{1}{2}}E_3/E$.	Per cent. diff.
Ag 47	Jönsson	5·25	5·15	1·9	5·05	4·0	4·68	4·01	16·7	4·36	7·3	3·98	3·22	23·6
	Kellström [6]	5·82		13·0		15·2	4·66		16·2		6·9	3·17		−1·6
Ba 56	Küstner	4·64	4·63	0·2	4·50	3·1	4·01	3·65	9·9	3·89	3·1	3·06	2·86	7·0
La 57	,,	4·27	4·57	− 6·6	4·44	−3·8								
Ce 58	,,	4·53	4·55	− 0·4	4·42	2·5	3·92	3·60	8·9	3·82	2·6	2·84	2·82	0·7
W 74	,,	3·99	4·30	− 7·2	4·03	−1·0	3·45	3·46	−0·3	3·48	−0·9	2·48	2·57	0·4
	Allen [7]	5·5		27·9		36·5								
Pt 78	,,	5·3	4·22	25·6	3·91	35·6								
	Backhurst	4·26		0·9		9·0	3·41	3·40	0·3	3·38	0·9	2·49	2·48	0·4
Au 79	,,	4·25	4·20	1·2	3·86	10·1	3·37	3·38	−0·3	3·34	0·9	2·52	2·45	2·9
	Küstner	3·78		−10·0		−2·1	3·28		−3·0		−1·8	2·47		0·8
	Dauvillier [8]	4·2		0·0		8·8	3·5		3·6		4·8	2·5		2·0
	Allen	5·2		23·8		34·7								
Hg 80	Uber	4·02	4·17	− 3·4	3·83	5·0	3·40	3·36	1·2	3·31	2·7	2·45	2·44	0·4
Tl 81	Küstner	3·64	4·14	−12·1	3·79	−4·0	3·15	3·34	−5·7	3·28	−4·0	2·36	2·42	−2·5
Pb 82	,,	3·70	4·12	−10·2	3·76	−1·6	3·21	3·32	−3·3	3·26	−1·5	2·38	2·40	−0·8
	Allen	5·6		35·9		49·0								
Th 90	Küstner	3·68	3·96	− 7·1	3·50	5·1	3·19	3·20	−0·3	3·02	5·6	2·27	2·23	1·8
U 92	,,	3·52	3·92	−10·2	3·44	2·3	3·05	3·18	−4·1	2·97	2·7	2·17	2·19	−0·9
	Stoner and Martin [9]	4		2·0		16·3								

Küstner found $J(L_1/L_2)$ and $J(L_2/L_3)$ to be constants, this requiring that both $J(L_1/M_1)$ and $J(L_2/M_1)$ should be proportional to $J(L_3/M_1)$. In consequence of the validity of equation (3), all three jumps should, to agree with his results, be proportional to E_3/E. The curves shown for $1{\cdot}11\,E_3/E$ and $0{\cdot}96\,E_3/E$ have constants chosen to give about the best agreement with Küstner's results, which they fit reasonably well. The findings of other authors for $J(L_1/M_1)$ are, however, seen to be (fig. 1) in better agreement with E_1/E than with $1{\cdot}11\,E_3/E$, but the experimental points are somewhat widely scattered for a definite inference to be drawn. The curve $0{\cdot}96\,E_3/E$ (fig. 2) appears to agree with the total experimental data rather better than $2^{-\frac{1}{4}}E_2/E$ for the (L_2/M_1) jump.

On the whole it seems necessary to conclude that, of the equations given above, only equation (3) can yet be regarded as fairly well established.

References.

(1) Jönsson, Diss. Upsala (1928).
(2) Backhurst, Phil. Mag. vii. p. 353 (1929).
(3) Uber, Phys. Rev. xxxviii. p. 217 (1931).
(4) Küstner, *Phys. Zeits.* xxxiii. p. 46 (1932).
(5) Siegbahn, 'Spektroskopie der Rontgenstrahlen,' 2nd edition, p. 346 (1931).
(6) Kellström, *Zeits. für. Phys.* xliv. p. 269 (1927).
(7) Allen, Phys. Rev. xxviii. p. 907 (1926).
(8) Dauvillier, *Comptes Rendus*, clxxviii. p. 476 (1924).
(9) Stoner and Martin. Proc. Roy. Soc. A, cvii. p. 312 (1925).

XXV. *Intensity of the Radiation from Uniform Columns in Discharge-Tubes. By* J. S. Townsend, *M.A., Wykeham Professor of Physics, Oxford, and* E. W. Townsend, *New College, Oxford* *.

1. THE intensity of the radiation from electric discharges in rarefied gases has been investigated by various methods, and in most cases the intensity of some part of the spectrum has been found in arbitrary units.

The object of this investigation is to determine the intensity of the radiation in absolute units from a uniform column, and to compare the amount of energy radiated

* Communicated by the Authors.

from the gas with the amount required to maintain the discharge.

The energy required to maintain the discharge in unit length of the positive column is $\cdot 24 \times X \times i$ calories per second, where X is the electric force in volts per centimetre and i the current in amperes. The force X may be measured by means of a calorimeter in the form of a cylinder with a steady flow of water round part of the discharge-tube. If the calorimeter be opaque the energy $\cdot 24 \times X \times i$ is absorbed by the water, but if the calorimeter is made of glass a smaller amount of heat is absorbed by the water. The difference between the amounts of heat absorbed by the opaque and transparent calorimeters gives a measure of the radiation from the gas that passes through the water and the glass tubing.

The difference between these two amounts of heat is too small to be measured accurately with currents of the order of 10 milliamperes in wide tubes containing gas at pressures greater than 3 or 4 millimetres, and it is necessary to use a thermopile to measure the energy of the radiation from the discharge.

This involves the calibration of the thermopile in such a manner that the radiation from unit length of the discharge may be given in absolute units by the galvanometer connected to the thermopile when the latter is at a distance of a few centimetres from the discharge-tube.

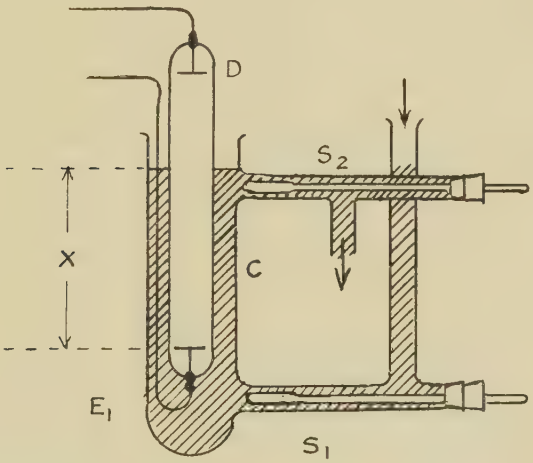
For this purpose it is desirable to have a long luminous cylinder as a standard source of uniform radiation, such that the energy radiated per unit length of the cylinder may be found in calories and adjusted to any required value.

A convenient source of radiation of this type is obtained by means of an incandescent lamp with a long straight filament, as the radiation from the lamp may be found in absolute measure by a transparent calorimeter.

2. The calorimeter used in these experiments is shown in fig. 1. It consisted of a glass tube C about 40 cm. long and 4·1 cm. internal diameter, with two side-tubes, S_1 and S_2. The axis of the tube C was vertical, and a steady stream of water flowed in through the tube S_1 and out through S_2. The discharge-tube D was fixed with its axis coinciding with that of the tube C. The lower

electrode E_1 was positive, and the upper end of the positive column was above the level of the water in the calorimeter. The change in temperature θ of the water that passed by the discharge-tube was given by the thermometers in the side-tubes. Thus if q be the volume of water passing through the calorimeter per second, the energy absorbed by the water is $q\theta$ and the energy supplied to maintain the discharge is $\cdot 24 \times V \times i$, V being the difference of potential between the electrode E_1 and a point P on the axis of the tube at the height of the water in the calorimeter.

Fig. 1.



In the uniform positive column the force X is constant except at points near the electrode and near the Faraday dark space, so that the potential V may be expressed in the form $V = V_0 + xX$, where V_0 is a constant and x the distance of the point P from the electrode E_1.

Thus if θ_1 and θ_2 be the changes in the temperature of the water when the electrode E_1 is at the distances x_1 and x_2 from the surface of the water in the calorimeter, the energy radiated per second from unit length of the positive column that passes through a transparent calorimeter is the difference between the quantities $\cdot 24 \times X \times i$ and $q(\theta_2 - \theta_1)/(x_2 - x_1)$.

If the calorimeter be opaque these two quantities are

equal, and the apparatus may be used to determine the force X and the potential V_0.

3. In order to determine these quantities experiments were made with a cylinder of copper foil on the inner surface of the calorimeter C. In this case all the energy from the discharge-tube is absorbed by the water in the calorimeter, V is given by the equation, $\cdot 24 \times V \times i = q\theta$, and the potential V_0 and the force X are obtained from determinations of the temperatures θ with the positive electrode at two different depths below the surface of the water in the calorimeter.

The following are the results of experiments which were made with a discharge-tube 2·9 cm. internal diameter containing neon at 3 millimetres pressure. With a current of 30 milliamperes in the tube and a uniform flow of water of 31·5 cubic centimetres per minute in the calorimeter the increase of temperature θ_1 was ·43° C. with the positive electrode 4 centimetres below the surface of the water, and the increase θ_2 was 1·18° C. with the electrode 21·5 centimetres below the surface. Thus $V_0 = 19$ volts and $X = 3 \cdot 13$ volts per centimetre. This value of X is in good agreement with Johnson's * determinations of the forces in direct current discharges in neon.

It will be observed that the cathode fall of potential may be found with the opaque calorimeter by measuring the increase of temperature when a point in the Faraday dark space is at the height of the surface of the water.

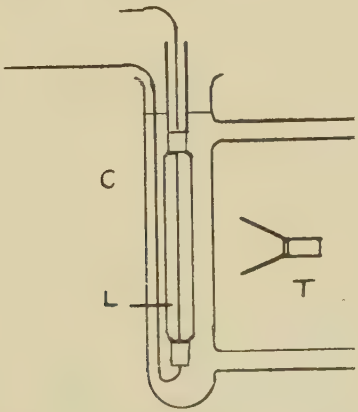
Experiments were also made with a similar tube containing helium at 4 millimetres pressure, and the force in the positive column was found to be 6·8 volts. per centimetre and the potential V_0 was 23 volts. When examined with a spectroscope there were no lines in the radiation due to impurities in either of the gases.

4. With currents of 10 or 20 milliamperes in these tubes the difference between the amounts of heat absorbed by the water in the opaque and transparent calorimeter is small and cannot be determined very accurately, but the radiation from the tube may easily be measured by a thermopile. For this purpose a " Moll " thermopile was used, with a sensitive galvanometer, and when the thermopile was placed with the cone 5 centimetres from the axis

* P. Johnson, Phil. Mag. x. p. 921 (Nov. 1930).

of the neon tube a deflexion of 20 millimetres was obtained on the galvanometer scale due to the radiation from the gas when a current of 10 milliamperes was passing through the tube. This effect was due principally to radiation in the visible spectrum, as the discharge-tube was of pyrex, which absorbed most of the ultra-violet radiation. The current in the thermopile attained a constant value a few seconds after the discharge was started in the gas, and did not increase when the discharge was maintained for some minutes. There was a glass plate in front of the thermopile which was impervious to long wave radiation from the pyrex when the temperature of the latter had

Fig. 2.



increased a few degrees after the discharge has been maintained for some minutes. When a rock-salt plate was substituted for the glass plate the current in the thermopile approached the constant value as before in a few seconds, but it increased gradually as the pyrex tube became heated by the discharge.

5. The arrangement of the apparatus used as a standard source of radiation for calibrating the thermopile is shown in fig. 2.

It consisted of the transparent calorimeter C with two side-tubes (as in fig. 1) and an incandescent lamp L, with a straight filament 25 cm. long in a tube 2·5 cm. in diameter. The lamp was completely immersed in the water of the calorimeter, and was fixed with the

filament coinciding with the axis of the calorimeter. The lamp was heated by a current of ·25 amperes with a potential of 100 volts, so that the energy supplied to the calorimeter was 360 calories per minute.

The apparatus was tested with a cylinder of copper foil on the inner surface of the tube C, and it was found that the amount of heat absorbed by the water was (360 ± 2) calories per minute.

With a constant flow of 62 c.c. per minute the temperature of the water in the transparent calorimeter was increased by 4·22° C., so that the water absorbed 262 calories per minute, and 98 calories per minute were radiated through the water and the calorimeter tube. Thus the energy radiated per unit length of the transparent calorimeter was $6{\cdot}5 \times 10^{-2}$ calories per second, which is much greater than that radiated from an ordinary discharge-tube.

When the thermopile was placed at a distance of 100 centimetres from the calorimeter the galvanometer deflexion was 193 millimetres, so it is necessary to reduce the radiation in order that the galvanometer deflexion may be of the same order as that obtained with the neon tube when the cone of the thermopile T (fig. 2) is 5 centimetres from the axis of the calorimeter.

A uniform reduction in the radiation in all directions from the calorimeter was made by placing a semi-transparent cylindrical screen round the lamp. It was found that the most convenient and effective method was to place one or two cylinders of coloured paper round the calorimeter. Thus with the thermopile at 100 cm. from the calorimeter the galvanometer deflexion of 193 mm. was reduced to 51 mm. with one screen, so that the energy radiated per second from unit length of the calorimeter was reduced to $1{\cdot}72 \times 10^{-2}$ calories. Further reduction was made by using two screens of different colours, and the radiation per unit length of the cylinder was thus reduced to $1{\cdot}41 \times 10^{-3}$ calories per second. With this intensity of radiation the galvanometer deflexion was 58 millimetres when the thermopile was 5 cm. from the axis of the cylinder.

6. The intensity of the radiation from the neon tube, which gave a galvanometer deflexion of 20 millimetres with the thermopile 5 cm. from the axis, was therefore $4{\cdot}8 \times 10^{-4}$ calories per second from unit length of the

positive column. In this tube the force X was 3·13 volts per centimetre, so that the energy required to maintain a current of 10 milliamperes was $7{\cdot}5 \times 10^{-3}$ calories per second in unit length of the positive column. Thus the energy radiated from the gas was 6·4 per cent. of the energy that maintained the current. The latter amount is the energy gained by electrons in moving in the direction of the force, and since the motion is steady the electrons lose this amount in the collisions with atoms of the gas. Thus in the neon discharge 6·4 per cent. of the energy lost by electrons in collisions is converted into the energy of the radiation that passes through the pyrex tube.

With the tube 2·9 cm. internal diameter containing helium at 4 millimetres pressure the deflexion of the galvanometer was 21 divisions with the thermopile 5 cm. from the axis and a current of 10 milliamperes in the tube. In this case the energy radiated per unit length of the positive column was $5{\cdot}1 \times 10^{-4}$ calories per second and the energy that maintained the current $1{\cdot}73 \times 10^{-2}$ calories. The energy of the radiation from this tube with helium at 4 millimetres pressure was therefore 3 per cent. of the energy that maintained the current.

Experiments were also made with a quartz tube 3·6 cm. in diameter containing helium at 4·6 millimetres pressure, in order to compare the energy of the radiation in the range of wave-lengths from about 2000 Å. to 3000 Å. with the total energy radiated from the discharge. With a current of 10 milliamperes in the discharge-tube and a quartz plate in front of the thermopile the galvanometer deflexion was 14·0 mm., and with a glass plate instead of the quartz plate the deflexion was 13·7 mm. The energy of radiation with wave-lengths from 2000 Å. to 3000 Å. which is absorbed by the glass is therfore very small compared with the total energy radiated from the discharge.

7. In the previous investigations with photoelectric cells it was found that with a given current in the discharge-tube the radiation from the uniform column diminished as the pressure increased. There are similar changes in the total energy radiated from the gas as measured with a thermopile. This is shown by an experiment with a discharge-tube of pyrex 3·4 centimetres internal diameter containing helium at 22 millimetres pressure.

With a current of 10 milliamperes in the discharge-tube and the thermopile at 5 cm. from the axis of the tube the galvanometer deflexion was 5·1 mm., which corresponds to a radiation of energy of $1{\cdot}22 \times 10^{-4}$ calories from unit section of the tube per second. The force in the positive column was 28 volts per centimetre, so that the energy of the radiation was ·18 per cent. of the energy ($6{\cdot}7 \times 10^{-2}$ calories) required to maintain the current.

In this tube one of the electrodes was movable, so that it was possible to find the force in the positive column by measuring the potentials required to maintain a given current with the electrodes at different distances apart.

(The force may be measured accurately by this method when the gas is at a high pressure, but it is not very reliable when the gas is at pressures less than 5 or 6 millimetres in tubes about 3 centimetres in diameter. With the lower pressures a change in the distance between the electrodes often causes a small change in the distribution of the current at one of the electrodes which affects the potential between the electrodes even when the current is constant.

At the lower pressures the method of measuring the force by a calorimeter is much more reliable since there is no change in the positions of the electrodes in the tube, and the results are independent of fluctuations in the cathode fall of potential due to changes of temperature.)

8. The measurements of the energy of the radiation from the tubes containing helium at 4 millimetres and 22 millimetres pressure obtained with the thermopile may be compared with the measurements of the changes in the intensity of the light in the visible spectrum due to changes of pressure obtained with photoelectric cells.

In one series of these experiments * the intensity of the radiation from high-frequency discharges in helium in a quartz tube 3·4 cm. internal diameter was determined in arbitrary units for a range of pressures from 38 millimetres to 1 millimetre. With a constant current in the tube the radiation from the uniform column increased as the pressure diminished, but the increase was not the same in the different parts of the spectrum. With the pressure 22 millimetres the force in the uniform column was 31 volts per centimetre, and the mean intensity

* J. S. Townsend and E. Llewellyn Jones, Phil. Mag. xii. p. 815 (Oct. 1931).

of the light that passed through the different filters was 14 in arbitrary units. With the same current in the discharge-tube and the pressure 3·4 millimetres the electric force was 6·3 volts per centimetre, and the mean intensity of the light was 53 in the same units. Thus the ratio of the energy of the radiation to the energy that maintained the current in the gas was increased by the factor 18·5 when the pressure was changed from 22 millimetres to 3·4 millimetres.

9. The particular pressure of 3·4 millimetres is chosen as one of the pressures in the above calculation, since the energy of agitation of the electrons in the tube 2·9 centimetres in diameter containing helium at 4 millimetres pressure is the same as in the tube 3·4 centimetres in diameter with the gas at 3·4 millimetres pressure. This follows from the theory of the discharge, which shows that the ratio X/p in the uniform column is a function of the product $p \times d$, where p is the pressure of the gas and d the diameter of the tube. The proportion of the energy required to maintain a discharge which is converted into energy of radiation by collisions of electrons with atoms of the gas should therefore be the same in the tube where $d = 2{\cdot}9$ cm. and $p = 4$ mm. as in the tube where $d = 3{\cdot}4$ cm. and $p = 3{\cdot}4$ mm.

With the former tube the ratio of the energy of the radiation to the energy that maintained the current as found with the thermopile is 3×10^{-2}, which is 17 times the ratio $1{\cdot}8 \times 10^{-3}$ obtained with the tube 3·4 centimetres in diameter with helium at 22 millimetres pressure. This is in good agreement with the factor 18·5 deduced from the experiments with photoelectric cells.

The large increase in the energy of the radiation thus found by both sets of experiments is due to the increase in the energy of agitation of the electrons. The mean energy E has been determined experimentally, and the values of $\overline{E}$ in the uniform columns of discharge may be obtained from the tables giving $\overline{E}$ in terms of ratio X/p. In the tube containing helium at 22 millimetres pressure the mean energy of agitation was 2·4 volts, and in the tube of the same diameter (3·4 cm.) with the gas at 3·4 cm. pressure the mean energy of agitation was 3·6 volts.

10. In order to find the proportion of the total energy $\cdot 24 \times X \times i$ that is radiated from discharges in helium at lower pressures in the tubes 3·4 centimetres in diameter

it may be assumed that the energy of the radiation is 3 per cent. of the total energy when the pressure is 3·4 millimetres, and at lower pressures the energies may be deduced from the values obtained in arbitrary units.

It is thus found that at 2·8 millimetres pressure 3·9 per cent. of the total energy is radiated, at 2 millimetres pressure 3·9 per cent., and at 1 millimetre pressure 10 per cent. The mean energies of the electrons are 3·6, 3·9, 4·3, and 5·3 volts at these four pressures respectively. Thus a considerable proportion of the energy required to maintain the currents in the uniform columns is converted into the energy of the radiation from the gas.

At these pressures the energy of the radiation is nearly all in the line spectrum of the gas, as no bands can be seen in the spectroscope and there were no lines except the helium lines.

There is therefore a considerable number of collisions in which the energies of the electrons are greater than the minimum energy required to excite lines in the visible spectrum, which is about 23 volts, even when the mean energy of the electrons is less than 4 volts. This shows that the energies are distributed about the mean, and the above numbers give evidence as to the law of distribution.

11. This conclusion is in general agreement with the results of the experiments on the motion of electrons in gases, where the mean energy of agitation of the electrons was found in terms of the ratio X/p. The mean loss of energy of the electrons in collisions with atoms was also determined. If E be the kinetic energy of an electron and λE the mean loss of energy in a collision with an atom of helium *, the coefficient λ was found to be nearly constant $\lambda = 2{\cdot}5 \times 10^{-4}$ when the mean energy of agitation $\bar{E}$ of the electrons was between ·4 volt and 3 volts. Thus within this range of values of E the loss of energy of an electron is nearly the same as the loss in a collision with an elastic sphere of the same mass as the atom of helium.

When the mean energy is greater than 3 volts the coefficient λ is increased. With the mean energies of 3·6, 3·9, 4·3, and 5·3 volts the values of $\lambda \times 10^4$ were 2·77, 2·85, 3·15, and 6·4 respectively.

These results led to the conclusion that the energies

* J. S. Townsend and V. A. Bailey, Phil. Mag. xlvi. p. 657 (Oct. 1923).

of the electrons are distributed about the mean energy, and the increase in the coefficient λ above the value $2{\cdot}5 \times 10^{-4}$ is due to losses of energy in large amounts in some of the collisions where the energy of the electron is greater than the energy required to excite the line spectrum of helium or ionize the gas.

It is unreasonable to treat the motion on the hypothesis that there is no appreciable distribution of the energies about the mean when the values of $\bar{E}$ are small, and to attribute the large values of λ to impurities in the gas.

It will be observed that the values of X/p, at which definite increases were obtained in the values of λ, are the same as the values of X/p in the discharge-tubes, where the energy of the radiation is about 3 or 4 per cent. of the energy required to maintain the current.

It is difficult to estimate the effect of large losses of energy in some of the collisions in the calculation of λ as the ordinary formula for λ is obtained on the hypothesis that there are no large abrupt changes in the energies of the electrons in the collisions with atoms. These losses are probably much greater than the loss represented by the amount of energy in the radiation as found by the thermopile. The theory of the line spectrum indicates that the lines in the visible spectrum are excited by the collisions, in which the electrons lose energy in the amounts of about 23 volts, but of this energy only a small proportion is converted into energy of radiation of long wavelengths (greater than 3000 Å units). Thus in a collison where the yellow line is excited the energy of this radiation is represented by 2·1 volts and the loss of energy of the electron is about 23 volts.* The remainder of the energy (23–2·1 volts) is converted into ultra-violet radiation, which does not pass through glass tubes or quartz tubes. It thus appears that the total loss of energy of the electrons, in the collisions in which radiation excited, is about ten times the energy of the radiation from the discharge-tube as received by a thermopile.

About 40 per cent. of the total energy acquired by the electrons under the action of the electric force would be lost in these collisions in the tubes 3·4 cm. in diameter containing helium at 2 millimetres pressure. With lower pressures nearly all the energy acquired by the

* W. Hanle, *Zeits. f. Physik.* lvi. p. 94 (1929).

electrons would be thus converted into the energy of the radiation in the ultra-violet and visible spectrum.

Under these conditions it is impossible to accept the laws of collisions founded on the hypothesis that metastable atoms are formed by collisions of electrons with normal atoms of helium, in which the electrons lose energy in the amounts of 19·77 volts, and that these collisions are much more numerous than those where the loss of energy is 23 volts and radiation is excited.

The energy lost in producing metastable atoms does not contribute to the radiation from the tube, and if most of the energy of the electrons were lost in producing metastable atoms it would be impossible to account for the energy received by the thermopile.

XXVI. *Notices respecting New Books.*

Almost Periodic Functions. By A. Besicovitch. (Cambridge University Press. Price 12*s.* 6*d.*)

THIS book divides sharply into its three main sections: (i.) Uniformly almost Periodic Functions; (ii.) Generalizations of almost Periodic Functions; (iii.) Analytic almost Periodic Functions. The first section begins the structural point of view involving the fundamental idea of translation numbers and develops the idea of Fourier coefficients and series for uniformly almost periodic functions, giving the Parseval equation. The section closes with an account of Approximation theory and Translation Number properties. The second section is devoted to a discussion of possible generalizations of Almost Periodic Functions and sets out their relationship with the corresponding convergence properties, while the final section deals with analytic almost periodic functions of a complex variable.

It will be seen at a glance that this volume serves a very useful purpose in that the first section forms, for new-comers to the subject, an introduction which gathers together in one place the results of the original papers on this subject, and it is agreeable to note that the proof of the main theorem has been reduced to a very convenient and manageable form. The second section is welcome in that it gives a unity to the generalization possibilities considered, and removes some of the apparent lack of cohesion in generalization theory.

Throughout the book has been carefully written and set up, with the point of view and convenience of the reader well

in mind. This is much to be commended in a subject in which it is easy for encyclopædic knowledge to produce obscurity and lack of interest. The author is to be congratulated on having presented an involved subject in a very acceptable manner.

Microenergetique. By PIERRE BRICOUT. [Two vols. 9″×5″, each pp. 300.] (Paris: Gauthier-Villars et Cie. Price 100 francs. Paper covers.)

THIS is a work which aims at an account, both theoretical and experimental, of the physics which has arisen as a result of the study of small-scale phenomena. A compact translation of the title is difficult to give: it is a work which covers the whole field of atomic physics and stresses the new attitudes which have been necessary in order to understand atomic phenomena. Such a book is one which physicists who seek to master the present day physical problems have been wanting for several years, and one cannot but congratulate M. Bricout on attempting a task which requires abilities of so diverse a kind.

There are two volumes, each of two parts. The first volume contains introductions, both mathematical and experimental, to the working out of the new principles and their application to the actual facts. The second volume develops the new principles and theoretical methods, and concludes with their operation in the explanation of experiment. The two volumes are, to a certain extent, independent, but a full understanding of the second volume requires knowledge of the first.

In the first volume the mathematics is given quite thoroughly, with no attempt to simplify it. It covers matrices, vectors and tensors, series of functions, calculus of variations, canonical equations, second order differential equations and quantum statistics—and is developed for its utility in modern physics. The chapter on Quantum Statistics is short and clear and stands alone, and is the best summary in book form the reviewer knows. For the rest—it is difficult reading to a non-mathematician, but would certainly repay the effort given to it. The experimental summary is comprehensive and easy to read—the account of modern developments in spectral interpretation, in particular, is compact yet sufficient.

The second volume shows the author's skill in exposition. The principles and methods are developed through generalized dynamics, and the unsatisfactory "classical" quantum mechanics to wave mechanics and matrix mechanics. Each chapter has a short introduction, in which the contents are

laid out ; and where the development has been long, summaries are given to fix the reader's ideas. There is no shortening of the reasoning which makes books such as this so difficult to read. Finally, the two new quantum mechanics are brought together and a short account of Dirac's general theory is given. The last book of all relates theory to fact. Some of this is familiar, but the chapters on electron diffraction, the spinning electron, molecules (including an account of the homopolar bond) and radioactivity are very welcome inclusions in a textbook. A short account of Born's collision theory is also an admirable insertion.

The printing and general arrangement are of the familiar type associated with French publications. A serious omission, particularly in Vol. I., is an alphabetical index.

No one who wished to acquire a true understanding of atomic physics could regret purchasing this work.

The New Background of Science. By Sir JAMES JEANS, D.Sc., F.R.S. [Pp. viii+303.] (Cambridge, at the University Press. Price 7*s.* 6*d.* net.)

THOSE who are familiar with Sir James Jeans's scientific writings will look forward with great pleasure to reading this volume. They will find in it one of the most successful expositions of the twentieth century revolution in physical science. Sir James has surpassed himself in endeavouring to give the general reader a knowledge of what is proceeding in the scientific world. He gives the present situation in broad outline and in the simplest possible terms, presenting it against "a background of rudimentary philosophy without which we can neither see our new knowledge as a consistent whole nor appreciate its significance to the full."

In the nineteenth century the physicist "thought of nature as an assemblage of objects located in space and continually changing with the passage of time." "He accepted a 'common-sense' view of nature, believing that there was no great difference between appearance and reality." "The old philosophy ceased to work at the end of the 19th century." "The 20th century physicist is hammering out a new philosophy for himself. Its essence is that he no longer sees nature as something entirely distinct from himself. Sometimes it is what he himself creates or selects or abstracts ; sometimes it is what he destroys." "We can only explore it by tramping over it and we raise clouds of dust at every step." "Each observation destroys the bit of the universe observed and so supplies knowledge only of a universe which has already become past history."

In certain aspects "Nature is like a rainbow . . . . . we now

know that the objective rainbow is an illusion . . . . . as the rays which enter one man's eyes can never enter those of a second man, no two men can ever see the same rainbow . . . . . And it is the same with the nature which each man sees. Again just as a man's rainbow follows him about as he moves round the country side, so nature follows us about. At whatever speed we move we find nature adjusting itself to our motion so that this motion makes no difference to its laws." Yet a rainbow has a background of distant forests and hills relative motion to which records our motion. " Physical science can find no such background for nature."

In this way the leading ideas of Heisenberg and Einstein are introduced.

Many Greek philosophers believed that matter consisted of hard indivisible pellets having all the characteristic properties of the substance constituting it. This hypothesis developed rapidly in the eighteenth and nineteenth centuries. Each pellet (or molecule) was found, however, to be divisible into atoms, and these have more recently been divided into protons and electrons having opposite electric charges. Newton had adopted a corpuscular theory of light, but it proved difficult to fit all the facts of observation into such a theory. Shadows of big objects are regions of protection formed as though light consisted of gun shot. But a small object affords no such protection: the behaviour now characterizes waves rather than projectiles. Throughout the nineteenth century the evidence for the wave theory seemed almost complete; this implies a sharp distinction between particles of matter and portions of radiation. Nevertheless, at the present day, radiation is " pictured as a crowd of photons moving equally and indiscriminately in all directions just as a gas in equilibrium may be pictured as a crowd of molecules."

In a similar way electrons which behave as particles in space produce diffraction effects in passing through plates. Thus light and electrons " can appear sometimes as particles and sometimes as waves, but *never as both at the same time.*"

The object of this volume is to give an exposition of the intricate theory which represents these complicated phenomena in non-mathematical terms, and to show how both the particles and wave-pictures of radiation may represent partial aspects of a unity which transcends both particles and waves.

It is impossible in a short notice to summarize the development of this thesis in Sir James Jeans's hands. He surmounts the difficulties of the subject and expounds the matter in a way which every student should read. The picture presented is a mathematical one, " as though in Boyle's phrase, mathematics is the language in which nature is written." But he does not

stop there as many investigators are doing; he declares his opinion that the fact that the search of a physical reality underlying the mathematical description of nature has so far failed does not, of course, imply that the search must for ever fail. "Who shall say what we may find awaiting us round the next corner?"

On p. 66 the word "not" is needed in the last line; on p. 227, near the middle, "protons" should be "photons."

The Universe of Science. By H. LEVY, Professor of Mathematics at the Imperial College of Science. [Pp. xii+224.] (London: Watts & Co. Price 7*s.* 6*d.* net.)

"A SOCIETY can remain stable only when its relative parts are geared to change at comparable speeds. Science, the driving power, has developed at its own pace without the evolution of a corporate conception of steady adjustment between the static and dynamic features of society as a whole."

Thus in its external aspects the scientific revolution seems to the author to be in an unsatisfactory state. But internally also things are not what they should be. "The age of rugged materialism that reached its zenith during last century is giving place to a new synthesis. The interpreters of the new knowledge and understanding, Sir James Jeans, Sir Arthur Eddington, Professor Millikan, General Smuts, to mention only a few, have almost without exception approached their problems against a background of outworn Idealist Philosophy none the less significant in its colouring because it has been unobtrusively though tacitly present."

It will be judged from the above extracts that Professor Levy is out of sympathy with much that is being hailed to-day as the most suggestive discoveries and pronouncements and interpretations of Science. He voices this dissatisfaction in the present book. We must confess, however, that, although he occasionally scores a point, he does not succeed in putting his case in such a way as to compel the conviction that he is even substantially right.

It should be borne in mind that the present mathematical movement is remarkably successful in connexion with the interpretation of the large increase in experimental knowledge which is simultaneously being made. Even those of us who are most cautiously inclined admit this success and look forward with hope to its developments in the future.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]